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AFML-TR-65-203

ADVANCEMENT OF PROTECTIVE COATING SYSTEMS FOR COLUMBIUM AND TANTALUM ALLOYS

J. D. Gadd
TRW INC.
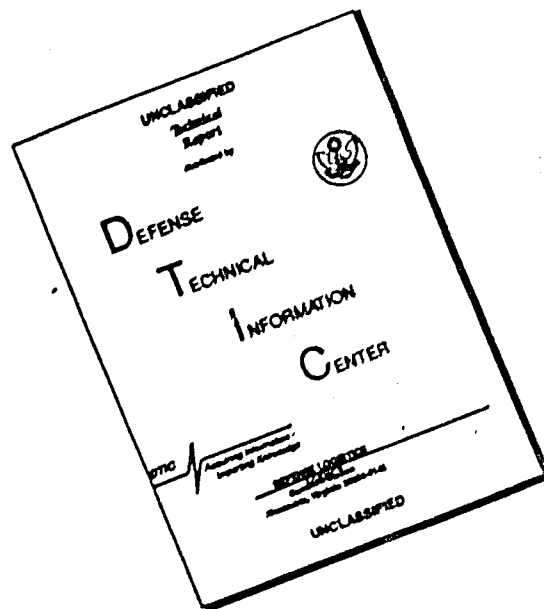Equipment Laboratories

TECHNICAL REPORT AFML-TR-65-203

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AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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6

**ADVANCEMENT OF PROTECTIVE COATING
SYSTEMS FOR COLUMBIUM AND
TANTALUM ALLOYS**

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FOREWORD

This report was prepared by Materials & Processes Department, TRW Equipment Laboratories, Thompson Ramo Wooldridge Inc. under USAF Contract No. AF 33(615)-1525. This contract was initiated under Project No. 7312, Task No. 731201. The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, with Lt. Paul Lane, Jr. acting as project engineer.

This report describes the results of the program conducted during the period 1 April 1964 to 1 April 1965. TRW has assigned to the report the No. ER 6486.

The project at TRW was managed by R. A. Jefferys and Dr. J. D. Gadd was the principal investigator. H. J. Tolchinsky assisted in the technical effort, E. H. Roland conducted the chemical vapor deposition studies and M. A. Borovic performed the electron microscopy analyses.

The manuscript of this report was released by the author June 1965 for publication as an RTD technical report.

This technical report has been reviewed and is approved.

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ii

ABSTRACT

A program was conducted to investigate and advance coating systems for the oxidation protection of columbium and tantalum base alloys. Four major areas of investigation were pursued: (1) a study of the basic factors associated with the diffusion formation and oxidation protection of the vacuum pack Cr-Ti-Si coating on columbium, (2) the laboratory scale development of a spray-diffusion process for application of the Cr-Ti-Si coating, (3) the development of metallic coating systems for the protection of columbium and tantalum materials to temperatures of 3500°F and (4) an oxidation and mechanical property aluation of various coating-base metal systems studied in the program.

In Phase I, Cr-Ti and Cr-Ti-Si coatings on unalloyed columbium, and D-43 B-66 alloys were studied in as-formed and oxidation tested conditions. As-coated specimens representing various time stages in the diffusion formation of the Cr-Ti-Si system were analyzed; and coatings were studied after various oxidation exposures at one atmosphere and reduced pressures. Electron microprobe, light and electron microscopy, and X-ray diffraction data are presented. Element concentration profiles are delineated; microstructural observations and phase identifications are discussed, and continuous oxidation weight change data are presented.

Phase II resulted in the laboratory scale development of a spray diffusion process capable of producing Cr-Ti-Si coatings comparable both microstructurally and in protective properties to the vacuum pack Cr-Ti-Si coating.

Two concepts were explored in the investigation of coating systems for the 2700-3500°F protection of columbium and tantalum materials: (1) alloy modification of the existing Cr-Ti-Si coating and (2) a barrier layer approach. Efforts to upgrade the temperature capabilities of the Cr-Ti-Si coating by alloying the silicide with tungsten and molybdenum were generally unsuccessful. The barrier layer approach involved interposing a bonded metallic layer of tungsten between the columbium or tantalum substrate and an oxidation protective silicide coating. Metallographic and oxidation test data are presented which demonstrate the excellent potential of this coating system.

A property evaluation of various coating-base systems was conducted in the final phase of the program. Metallographic, oxidation and mechanical property test data are presented for various pack and slurry processed Cr-Ti-Si coatings on columbium and tantalum materials. A statistical analysis and Weibull treatment of the oxidation test data is presented. For testing at 2500°F, The Cr-Ti-Si coating evidenced 97.5% probably protective lives (99% confidence level) of 59 and 82 hours on D-43 and B-66 alloys, respectively.

TABLE OF CONTENTS

iv

TABLE OF CONTENTS

ILLUSTRATIONS

ILLUSTRATIONS

ILLUSTRATIONS

ILLUSTRATIONS

ILLUSTRATIONS

x

ILLUSTRATIONS

xi

ILLUSTRATIONS

TABLES

xiii

TABLES

TABLES

1. INTRODUCTION

It is well recognized that the inherently poor oxidation resistance of the refractory metals precludes their utilization in high temperature oxidizing environments in the absence of surface protection. The Air Force Materials Laboratory has sponsored numerous programs designed to develop, evaluate and advance high temperature protective coatings for the refractory metals in an effort to exploit their strength potential. Two such programs completed at TRW under Contracts AF 33(616)-7215 and AF 33(657)-7396 were successful in bringing forth a reproducible coating process and a reliably protective Cr-Ti-Si alloy coating for columbium base materials. In the course of these programs considerable data were generated characterizing the protective capabilities of the Cr-Ti-Si system on a majority of the available columbium base materials, over the temperature range 1200-3000°F. Certain limitations inherent in the coating and coating process were brought to light by these efforts. Thus, in the current program, emphasis was directed towards: (1) seeking a more fundamental understanding of the formation and protective nature of the Cr-Ti-Si coating, (2) investigating modifications in the basic coating process to improve process versatility, and (3) exploring the development of new coating systems for the protection of columbium and tantalum alloys at temperatures of 3000°F and above.

One of the primary objectives of the program was to conduct an analysis of the vacuum pack formation of the Cr-Ti-Si coating on three columbium base materials (unalloyed columbium, D-43 and B-66 alloys), utilizing metallographic, X-ray diffraction, electron microscopy, X-ray spectroscopy and electron microprobe techniques. An effort was made to (1) delineate the various stages in the formation of the Cr-Ti-Si coating, (2) identify phases and compositions across the many stratified coating layers, and (3) correlate morphological aspects of the alloy microstructures with both one atmosphere and reduced pressure modes of coating protection and failure.

Secondly, an investigation was conducted to develop a cold spray-diffusion process which would permit application of the Cr-Ti-Si coating on columbium base substrates in the absence of a massive granular coating pack. Very encouraging results were obtained in this effort, and the feasibility of applying the Cr-Ti-Si coating by a slurry process was well demonstrated.

The third principal effort in the program involved the development of oxidation protective coatings for both columbium and tantalum base materials for applications at temperatures up to 3500°F. One approach entailed an attempt to upgrade the temperature capabilities of the existing Cr-Ti-Si

1

system for performance on both tantalum and columbium base substrates at temperatures up to 3200°F. The experiments involved compositional modifications of the basic Cr-Ti-Si system by the addition of alloying elements to the silicon coating pack. However, for the protection of columbium and tantalum base materials at temperatures above 3200°F, a barrier layer coating concept was considered more promising. Barrier layers of tungsten and molybdenum were formed on columbium and tantalum substrates by various pack and vapor deposition processes. The outer portion of the barrier was converted to a protective coating by diffusion alloying with silicon, thereby forming an oxidation resistant disilicide coating. The duplex coating systems were evaluated by cyclic oxidation at temperatures to 3500°F.

The final phase of the program involved a mechanical property and oxidation evaluation of the various coatings studied in the earlier phases of the program. This included: (1) a reliability study of the cyclic oxidation protective properties of both pack and slurry applied Cr-Ti-Si coatings on columbium alloys, (2) tensile tests of pack and slurry Cr-Ti-Si coated D-43 alloy, (3) oxidation-creep tests of pack and slurry Cr-Ti-Si coated D-43 alloy and (4) hot gas erosion tests of pack Cr-Ti-Si coated columbium alloys.

2. SUMMARY

This report summarizes the results of a one year research and development effort under Contract AF 33(615)-1525. The major areas of investigation in this program were: (1) a fundamental study of the formation and protective mechanisms associated with the vacuum pack Cr-Ti-Si coating system on columbium, (2) the development of a slurry-diffusion process for the formation of the Cr-Ti-Si coating on columbium and (3) the development of coating systems for the protection of columbium and tantalum base materials at temperatures to 3500°F.

The analysis of the vacuum pack Cr-Ti-Si coating initially involved the preparation of Cr-Ti and Cr-Ti-Si coated columbium alloy coupons which represented various time stages in the diffusion formation of the Cr-Ti-Si surface alloy layer. Temperature probes were conducted to delineate the heat-up rates internally in the granular coating packs. Extensive metallographic studies were performed to determine the rates of coating formation, and to observe the changing microstructures as the diffusion process progressed. Electron microprobe, electron microscopy and X-ray diffraction studies were performed on representative specimens to describe the compositional and morphological characteristics of the Cr-Ti-Si coating.

It was shown that during the initial Cr-Ti coating cycle the Cr-Ti alloy overlay and diffusion zone form at essentially equivalent rates. The overlay portion of the coating is a Laves phase of the form $(Cb,Ti)Cr_2$ with an fcc $MgCu_2$ type structure. In some cases the Laves phase contains a precipitate of β titanium, particularly on D-43 alloy. Beneath the overlay is a substrate diffusion region containing chromium and titanium in solid solution.

2

Siliconizing of the Cr-Ti coating resulted in the formation of a disilicide coating of the form $(Cb,Cr,Ti...)Si_2$, which evidenced several distinct phase boundaries representative of various relative concentrations of Cr, Ti and Cb. Beneath the disilicide region were lower silicide bands of the form $(Cb,Cr,Ti...)_3Si_2$ and $(Cb,Cr,Ti...)_5Si_3$, and beneath these a solid solution region comprised of Cr,Ti and Si dissolved in the columbium matrix.

Analytical and microstructural studies were also conducted on several Cr-Ti-Si coated D-43 alloy specimens after oxidation exposure of the coupons at one atmosphere and at reduced pressures. At one atmosphere coated specimens were exposed for 100 hours at 1800°F, 4 and 50 hours at 2500°F and 4 hours at 2700°F. The reduced pressure exposure conditions were 1 and 4 hours at 2500°F, at 1 and 10^{-2} mm pressures. Electron microprobe analyses of these specimens indicated that under all of the above exposure conditions, chromium and titanium from the disilicide migrated rapidly to the free surface of the coating. During the initial period of exposure the major oxide on the coating surface was Cr_2O_3. Chromium subsequently vaporized from the surface, either as chromium or chromium oxide, eventually leaving an oxide scale rich in titanium and silicon, and ultimately in columbium. At the reduced pressures silicon also vaporized from the coating as the volatile SiO phase, resulting in a progressive recession of the coating surface. The majority of the unoxidized coating remained as a disilicide, although distinctly different disilicide regions were delineated with changing concentrations of chromium, titanium and columbium. Three factors contributed to the ultimate failure of the Cr-Ti-Si system: (1) loss of chromium from the coating, (2) enrichment of the disilicide and subsequently the protective oxide with columbium and (3) depletion of the chromium and titanium from the substrate solid solution (diffusion zone).

Electron microscopy, X-ray diffraction and continuous oxidation weight change data are also presented to supplement the light microscopy and electron microprobe analyses.

A reliability analysis of the protective capabilities of the Cr-Ti-Si coating on D-43 and B-66 alloys was conducted with 420 test coupons. On D-43 alloy these data represented a 100% reliability for 144 hours life at 1800°F, a 97.5% (99% confidence level) probability of 59 hours life at 2500°F and a mean protective life of 39 hours (from Weibull plot) at 2700°F. The analogous lives of the coating on B-66 alloy were 144, 82 and 33 hours, respectively.

A laboratory scale process was developed for the formation of the Cr-Ti-Si coating on columbium base materials by a slurry-diffusion technique. The process is two cycle, and entails the spray deposition of a halide activated metal slurry on the substrate, followed by diffusion treatment under

3

a partial pressure of argon. As in the vacuum pack process, the Cr-Ti coating is formed initially, followed by siliconizing; and the coatings are formed by vapor-solid diffusion reactions. Cr-Ti-Si coatings produced by this process were comparable both microstructurally and in protective capability to coatings formed by the vacuum pack process. Efforts to duplicate the slurry-diffusion coating in a pilot scale coating furnace were moderately successful, however, problem areas associated with process scale-up were revealed. Light micrographs and extensive cyclic oxidation data are presented in conjunction with the discussion of the slurry process development. A Weibull treatment of the cyclic oxidation data is also presented.

A series of mechanical property studies were performed to evaluate the relative influences of the pack and slurry Cr-Ti-Si coating processes on the properties of D-43 alloy. Tensile and creep test data are presented which demonstrate that the two processes affect comparable changes in the mechanical properties of as-received D-43 alloy sheet.

Arc plasma tests were conducted on various Cr-Ti-Si coated columbium alloy sheet specimens at temperatures to 3100°F. Photographs and post oxidation test data are presented. Cr-Ti-Si coated D-43 and B-66 alloy coupons were also oxidation tested in accordance with a profiled (slow) heating and cooling cycle. The severity of the slow thermal cycle, in contrast to conventional thermal cycling, is exhibited and discussed.

A cursory study was also made of the applicability of the Cr-Ti-Si coating on tantalum base materials. Metallographic results and oxidation test data are presented which indicate the coating system will protect tantalum base material, but currently at a level of reliability inferior to that exhibited by the coating on columbium.

A major area of investigation in this program involved the development of higher temperature protective coatings for tantalum and columbium base materials. Two approaches were pursued: (1) modification of the existing Cr-Ti-Si system for improved high temperature performance and (2) the development of duplex, barrier coating systems. Modification of the Cr-Ti-Si system entailed efforts to alloy the silicide with higher melting elements such as tungsten and molybdenum, by the addition of these elements to the silicon coating pack. The objective of this modification was that of up grading the refractory properties of the silicide coating and subsequently the protective oxides. In general these efforts were unsuccessful, although little evidence of appreciable alloying of the silicide was found.

The barrier layer concept involved the interposition of a high melting point element such as tungsten or molybdenum between the columbium or tantalum substrate and a protective silicide coating. Attempts to form this layer on columbium or tantalum by the vacuum pack process were unsuccessful, owing to the relatively low diffusion rates between the refractory metals.

4

Chemical vapor deposition was considered the most promising technique for the application of tungsten or molybdenum coatings, and several independent organizations engaged in the preparation of barrier layer coatings (NBS, Ethyl Corporation, GT&E and TRW) for this program. Tungsten coatings 1.5 mils thick were successfully deposited by GT&E; and these coupons were silicided with Si-(W) and subsequently oxidation tested. The potential of the barrier layer coating system was well demonstrated, with protective lives such as > 16 hours at 3000°F, >12 hours at 3200°F, > 4 hours at 3300°F and 2 and 3 hours at 3400 and 3500°F.

Several conclusions derived from an analysis of the data generated in this program are presented at the conclusion of the report.

3. MATERIALS AND TEST PROCEDURES

3.1 Materials

Four columbium base materials (D-43, B-66, Cb-752 alloys and unalloyed columbium) and two tantalum base substrates (Ta-10W alloy and unalloyed tantalum) were employed in the coating development studies. The chemical analyses for these various sheet materials are given in Tables 1 and 2.

3.2 Test Procedures

Cyclic oxidation tests, hot gas erosion experiments and mechanical property tests were utilized in evaluating the various coating-base metal systems investigated in this program. The majority of these test procedures will be described in the section of the report in which the data are presented. However, since cyclic oxidation tests (air - one atmosphere) were employed in various phases throughout the program, a description of the oxidation test procedures is appropriate at this point in the report. Table 3 presents a summary of these oxidation test procedures.

At temperatures from 1800-3000°F coated coupons were oxidation exposed in resistance heated (silicon carbide element) box furnaces. At 1800-2800°F the test coupons were supported on either high purity Al$_2$O$_3$ or fused quartz. Fused quartz proved superior to Al$_2$O$_3$ at 2500-2800°F, owing to its lesser tendency toward reaction with the coating, thus it was used exclusively as the support media at these temperatures in the latter portion of the program. The reactions which occur between the protective coatings and refractory support materials preclude the use of refractories at test temperatures of 3000°F and above. Sacrificial molybdenum pads protected with the Si-(W)[1] coating were successfully employed as the support media at the higher test temperatures. For testing in the temperature range 1800-3000°F thermal cycling involved air cooling of the coupons to approximately room temperature for visual inspection. The exposure interval between cycles was decreased with increasing test temperature for improved accuracy in detecting the time of coating failure, since the protective lives of the coatings were

5

TABLE 1

Chemical Analyses of Columbium Alloy Sheet Materials

Alloy	Heat No.	Thickness Mils	Source	Analysis-ppm(1)											
				O	K	N	C	Fe	Ti	W	Mo	V	Zr	Ta	Cb
D-43	43-383	30	Du Pont	296	4	42	910	-	-	11.2%	-	-	0.98%	-	Bal.
D-43	43-469	42	Du Pont	50	1	37	894	-	-	9.7%	-	-	0.92%	-	Bal.
D-43	43-387	50	AF	136	3	40	1070	-	-	9.4%	-	-	1.0%	-	Bal.
B-66	DX-603	30	Westinghouse	81	-	75	40	-	-	-	4.6%	4.9%	0.92%	-	Bal.
B-66	DX-625	50	Westinghouse	187	-	88	27	-	-	-	5.2%	5.0%	0.85%	-	Bal.
Cb-752	52207	30	Union Carbide	140	7	117	3	-	-	9.90%	-	-	2.90%	-	Bal.
Cb-752	52265	30	Union Carbide	67	2	28	50	-	-	10.05%	-	-	2.74%	-	Bal.
Cb	10-275	60	Du Pont	99	1	32	26	-	-	100	-	-	50	500	Bal.
Cb	89B-748	30	Fansteel	30	-	50	50	70	50	100	-	-	50	600	Bal.

(1) ppm - unless otherwise noted as weight percent (%)

6

TABLE 2

Chemical Analyses of Tantalum Base Materials

	Analysis - ppm[1]	
	Ta-10W (30 Mils)	Unalloyed Tantalum (30 Mils)
Elements	Heat No. 2549	Heat No. 69B867
O	23	70
H	–	5
N	17	20
C	14	50
Fe	10	–
Ti	10	–
W	10.4%	100
Mo	10	–
Cr	5	–
Cu	1	–
Zr	–	100
Mn	–	50
Ni	5	50
Al	50	50
Si	100	100
Sn	–	50
Ta	Balance	99.90%
Cb	100	300

(1)   ppm unless otherwise noted as weight percent

    Source - Ta-10W - NRC
              Ta - Fansteel

TABLE 3

Procedures for Cyclic Oxidation Testing Coated Columbium and Tantalum Materials in Air (1 Atmosphere) at Temperatures from 1800-3600°F

Test Temperature Range	Thermal Cycling Procedures Time Sequence	Cooling Range	Specimen Support Material	Type Test Furnace
1800-2500°F	One cycle per hour for 8 hours - 16 hours static per 24 hour period	RT	Al₂O₃ or Fused Quartz	Globar element
2700-2800°F	One cycle per hour to failure	RT	Al₂O₃ or Fused Quartz	Globar element
3000°F	Two cycles per hour to failure	RT	Si-(W) coated Mo sacrificial pad(a)	Globar element
3200-3600°F	Two cycles per hour to failure(b)	∿1000°F	Si-(W) coated Mo sacrificial pad(a)	Induction heated ZrO₂ tube furnace

(a) Specimen supported on Si-(W) coated Mo coupons, which were in turn supported on ZrO₂

(b) Continuous observation possible with optical pyrometer

8

considerably shorter at the higher temperatures. It was observed that during exposure at temperatures above 3000° F the columbium test coupon and molybdenum sacrificial pad became firmly bonded together by interdiffusion of the oxidized coatings. Upon cooling to near room temperature the differential in thermal expansion between the two systems was sufficient to fracture the bond, and both coating systems were severely damaged. Failures attributed to this origin would obviously not be representative of the capabilities of the protective coating under evaluation. Thermal cycling from the 3000-3400° F test temperatures therefore involved cooling of the coupons only to approximately 1000° F, although it is recognized that this less severe condition may have influenced the absolute protective lives exhibited by the coatings at these temperatures. The relative performance of the various coating systems should, however, be essentially unaffected by this condition. The tests at 3100° F and above were conducted in an induction heated ZrO_2 tube furnace, and continuous observation of the test coupons was possible with an optical pyrometer.

4. Cr-Ti-Si COATING SYSTEM ANALYSIS

A great deal of developmental effort has been devoted to advancing the Cr-Ti-Si coating system over the past few years; and the results of these efforts are manifest in the reliable and outstanding protective performance exhibited by this coating system on columbium base materials. For the most part, these development programs have emphasized: (1) optimization of the coating process parameters, (2) extensive performance evaluation of the coating and (3) advancement of the process versatility and applicability. Very little effort has been directed towards elucidating the basic factors which underlie the formation and protective performance of the Cr-Ti-Si coating on columbium base materials. Such a characterization was the objective of Phase I of this program.

Previous studies have indicated that the protective capabilities of the Cr-Ti-Si coating are markedly dependent upon coating composition. This was clearly evidenced by the results of the coating reliability study conducted under Contract AF 33(657)-7396[2]. Wide variations in protective properties were exhibited by coatings processed in the same coating pack, but in different regions of the retort. The time-temperature-pressure relationship was non-uniform throughout the retort, and the attendent heterogeniety of the coating vapor phase reflected in coatings of widely differing protective properties.

The initial approach to this problem involved the preparation of Cr-Ti-Si coatings which were representative of various time stages in the formation of the diffusion alloy coating. Specimens of three columbium alloys were located in two positions in the pack, and coatings were formed on these alloys employing two different Cr-Ti coating cycles and one siliconizing cycle. Temperature probes were conducted with thermocouples imbedded in the granular coating packs, and metallographic analyses were

9

performed for the determination of coating formation rates. As formed coatings were studied utilizing light microscopy, electron microscopy, electron microprobe and x-ray diffraction techniques. Similar coated specimens were subsequently exposed under various elevated temperature conditions (both one atmosphere and at reduced pressures), and the above analytical tools were again employed for comparative microstructural studies. The results of the studies are discussed in the subsequent text, and a summary of the analyses is presented at the conclusion of Section 4.

4.1 Specimen Preparation

4.1.1 Procedure

The coating work was performed in an induction heated vacuum furnace utilizing a 7 1/2" diameter x 18" high retort. Three columbium base materials were employed: unalloyed columbium, B-66 and D-43 alloys. All specimens were 1/2" x 1/2" sheet coupons, prepared by (a) shearing, (b) abrasive tumbling and (c) chemically etching in an aqueous solution containing 50% HF, 25% H_2SO_4, 10% HNO_3 and 15% H_2O.

To study the relative effect of retort location on coating formation, two positions within the pack were selected for specimen placement. These were the mid-radius positions inside the coating pack at: (1) the vertical mid-level of the retort and (2) five inches above the retort center. These positions correspond to the two upper levels employed in coating the materials for the previously referenced reproducibility and reliability analysis of the Cr-Ti-Si coating[2].

In order to analytically and optically study coatings which were representative of various time stages in the formation of the Cr-Ti-Si system, individual Cr-Ti and Si coating runs were terminated at various time intervals prior to completion of the coating cycle. Two basic cycles were employed in the formation of the initial Cr-Ti coating: (1) direct heating of the furnace to 2300°F and controlling at this temperature for 8 hours, and (2) heating the furnace to 2000°F, holding at this temperature for 4 hours, and subsequently elevating the temperature to 2300°F for an 8 hour coating period. The objective in using the latter processing cycle was twofold. First was an attempt to preferentially diffuse titanium into the columbium substrate at the lower temperature, thereby aiding the diffusion of chromium in this substrate region during the subsequent 8 hours at 2300°F. On a thermodynamic basis, at the lower hold temperature, the halide should react preferentially with the titanium in the Cr-Ti pack alloy. If a titanium precoat could be accomplished by this technique, the reduction in the melting point of the substrate surface layer by titanium enrichment would serve to enhance the subsequent diffusion of chromium in this substrate region. Secondly, the hold treatment definitely decreased the thermal gradient in the coating pack before the retort was heated to the coating temperature. This procedure should promote both coating

10

thickness uniformity and reproducibility at various locations throughout the retort. The termination times for the Cr-Ti coating cycle were 0, 3, 5 and 8 hours at 2300°F. These time-temperature schedules are shown schematically in Figure 1.

A basic cycle of 6 hours at 2100°F was used for the siliconizing treatment, and involved termination times of 0, 2, 4 and 6 hours at 2100°F. The processing parameters representative of complete coating cycles are summarized as follows:

Parameters	Cr-Ti Cycle	Siliconizing Cycle
Pack Composition - w/o	60Cr-40Ti	Si
Activator - w/o	0.5 KF	1.0 KF
Temperature - °F	2300*	2100
Time - Hours	8*	6
System Pressure - mm	10^{-2}	10^{-2}

* With and without 4 hour preheat at 2000°F

4.1.2 Retort Temperature Probe Analysis

In all coating development work in the induction heated vacuum furnaces, the furnace temperature was controlled by a thermocouple located at the mid-point level outside the retort, between the retort wall and the furnace susceptor. For this study the furnace and retort temperatures were also simultaneously monitored at three other locations. One thermocouple was located in the pack, adjacent to the specimens, at the center mid-radius position; a second in the pack at the top mid-radius position; and a third outside the retort at the top level between the retort and the induction heated susceptor.

Figure 2 shows the temperature profiles obtained with the 7 1/2" diameter x 18" high retort for a typical Cr-Ti coating cycle. In this case the furnace was heated directly to 2300°F, based on the response of the control couple located outside the pack at the vertical mid-point position. The temperature at the external top of the retort is observed to lag the middle position control temperature by approximately 100°F during heat-up. Once the control couple reached the coating temperature the input power to the furnace was reduced. Since the greatest heat loss occurred from the top of the retort (least insulation), and since the peak temperature of the susceptor was lower for the reduced input power, the external temperature at the top of the retort correspondingly decreased.

The internal pack temperature at the mid-radius position lagged the control thermocouple by approximately 1400°F at the instant the control couple reached 2300°F, indicating the low thermal conductivity of the granular pack. Of note also is that while the internal temperature at the

11
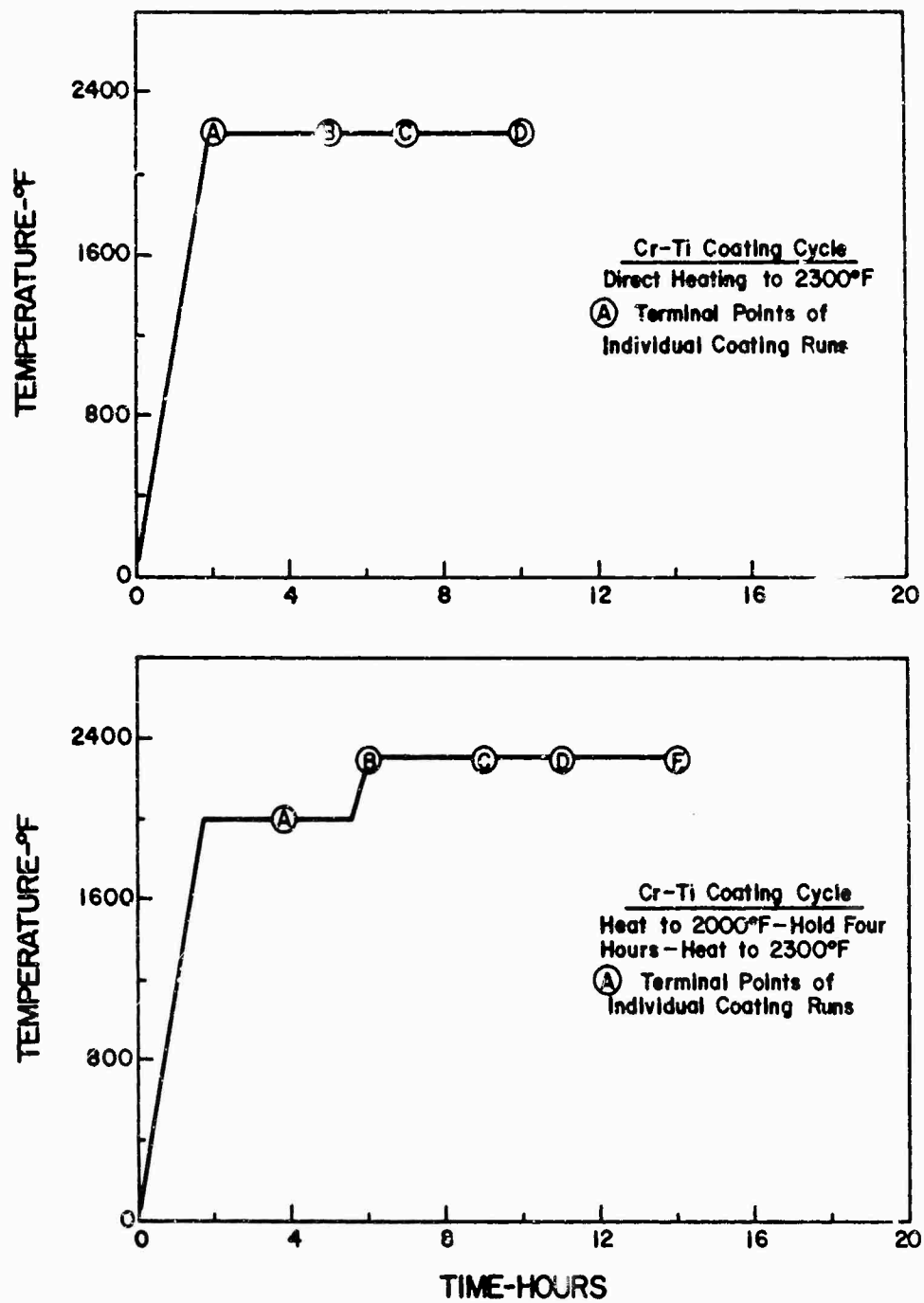
Figure 1   Schematic Time-Temperature Schedules for Study of Cr-Ti Coating
Formation

12
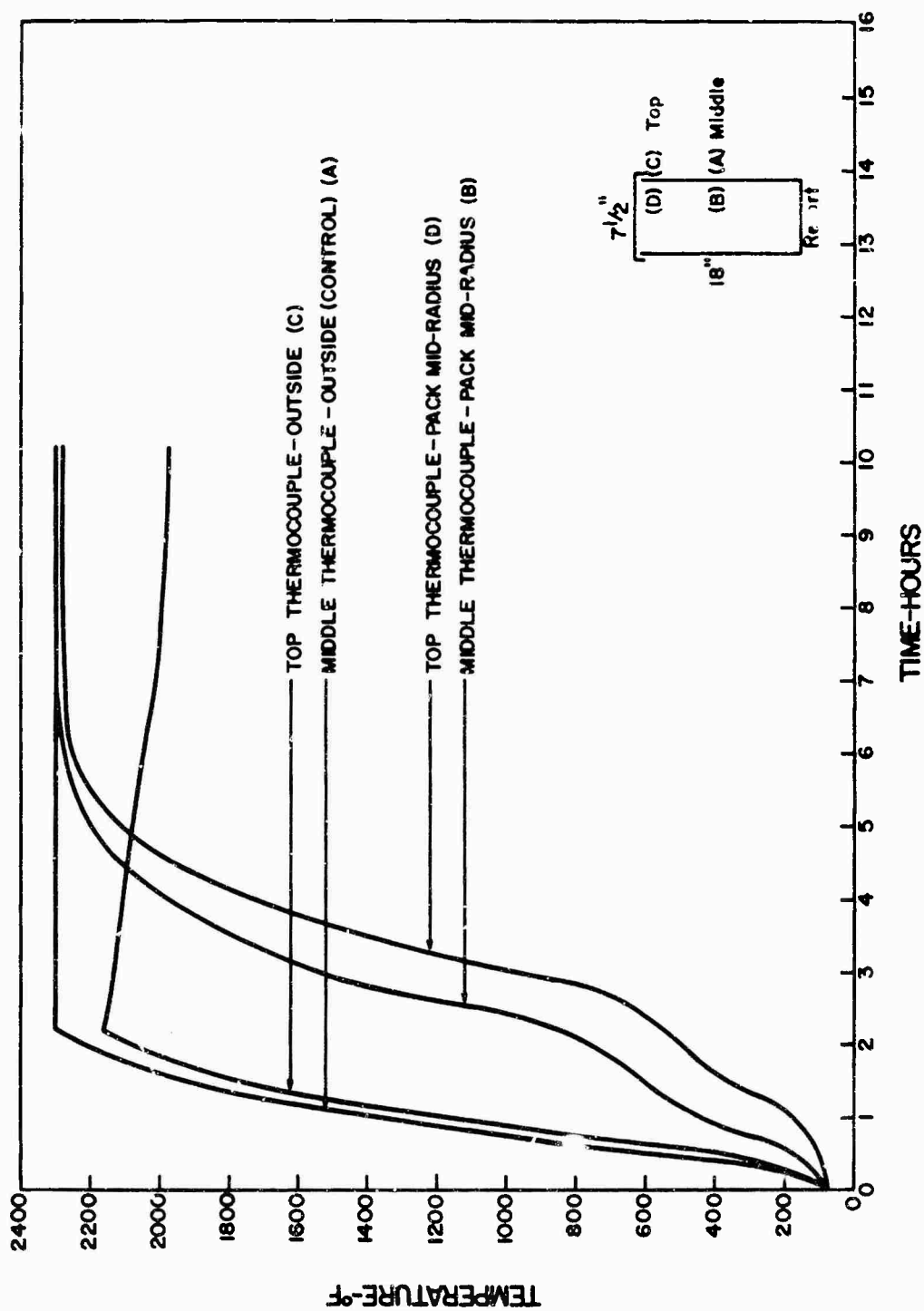
Figure 2 Temperature Profiles for 7 1/2" Diameter x 18" High Retort Involving Direct Heating of the Cr-Ti Pack to the Coating Temperature (2300° F)

13

retort top lagged the middle temperature for a considerable period of time, this differential decreased once the middle of the pack reached 2300°F. Apparently as the activator volatilized the conductivity within the pack improved. The most significant observation is, however, that the internal pack positions at which the temperature was monitored were at the coating temperature for only 3-4 hours of the 8 hour coating cycle.

Figure 3 shows the temperature profiles obtained for the coating cycle in which the 4 hour 2000°F hold treatment was employed prior to the 8 hours at 2300°F. As shown in this graph, the internal thermocouple at the vertical center of the pack recorded 2300°F just 2 hours after the control couple had reached the set temperature. In contrast, the internal couple lagged the control couple 4-5 hours when direct heating of the furnace to 2300°F was employed. Even with the hold cycle, however, the internal temperature at the top of the pack was approximately 50°F below that attained at the corresponding vertical mid-point location after the furnace reached thermal equilibrium. The influence of this hold treatment on the resulting Cr-Ti coatings will be discussed in a subsequent section.

Figure 4 is a plot of the analogous thermal profiles obtained with the silicon coating pack. The furnace was heated directly to 2100°F (control thermocouple) and maintained at this mean temperature for 6 hours. The rate of temperature increase internally in the pack, at the retort top position, is observed to exceed the corresponding temperature rise at the retort middle location. This trend is the reverse of that observed with the Cr-Ti alloy pack, and is apparently associated with the higher thermal conductivity of silicon and the relative effect of heat input through the retort top.

Approximately 3 hours of the 6 hour coating cycle was required for the internal mid-radius pack locations to reach the furnace control temperature. Although the internal temperature rise at the retort top exceeded that of the retort middle during furnace heat-up, the greater heat loss at the furnace top reflected in lower external and internal equilibrium temperatures during the latter stages of the coating cycle. Upon reaching the control temperature (2100°F) the temperature differentials between the internal and external thermocouples at the retort top and middle were 600 and 1400°F, respectively. The analogous temperature differentials in the Cr-Ti coating pack were 1600 and 1400°F. Two basic differences are noted between the temperature profiles for the Cr-Ti and silicon coating cycles: (1) the silicon pack heats internally about 25% faster than the Cr-Ti pack, and (2) the relative rates of temperature rise in the top and middle internal regions of the two metallic packs are reversed. The relationship between the thermal profiles and the various stages in the formation of the Cr-Ti-Si coating will be discussed in a subsequent section.

4.1.3 Preliminary Oxidation Tests

In view of the considerable time and effort being devoted to the

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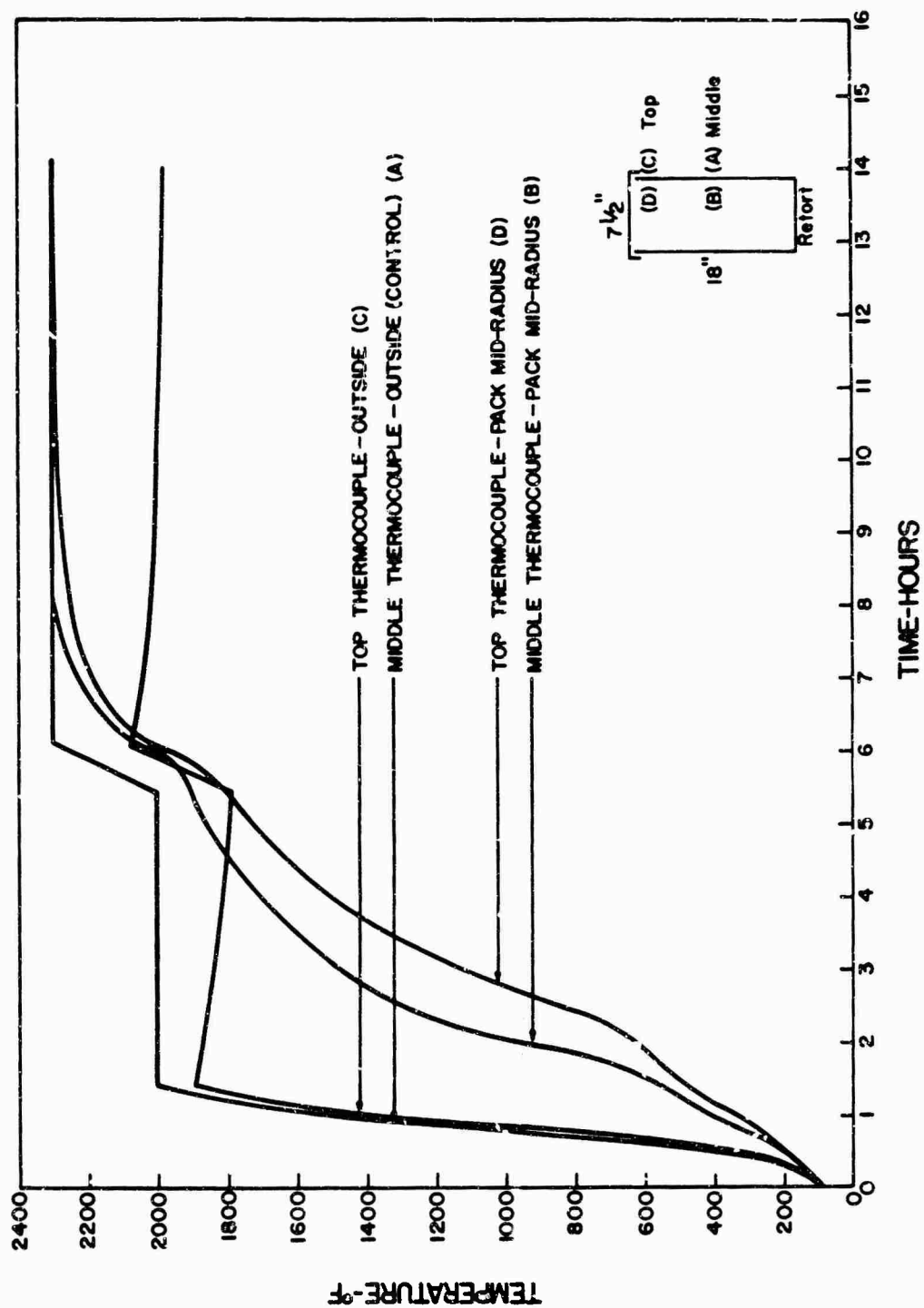
Figure 3 Temperature Profiles for 7 1/2" Diameter x 18" High Retort, Cr-Ti Pack, Intermediate Hold (2000° F) During Heat Up Cycle
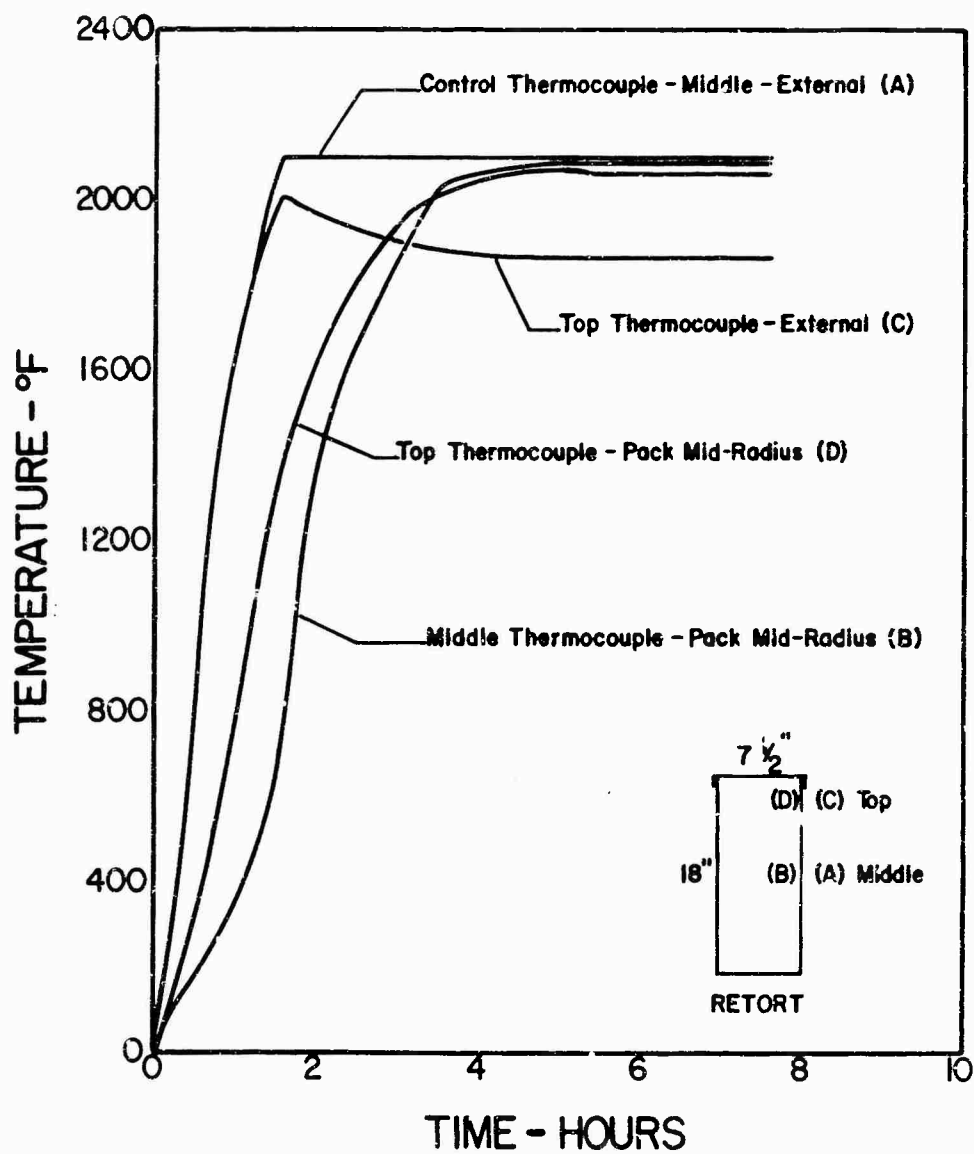
Figure 4 Temperature Profiles for Silicon Coating Cycle - Four Thermocouple
Locations - Retort 7 1/2" Diamet~. x 18" High

16

analysis of the Cr-Ti-Si coating in this program, it was felt that a group of coupons should be oxidation tested to ascertain the quality of the specific coatings being studied. Cr-Ti-Si coatings were therefore formed on 50 coupons each of B-66 and D-43 alloys, in conjunction with the preparation of the specimens for the optical and analytical analyses. The processing parameters and cyclic oxidation test results are presented in Table 4. The initial Cr-Ti overlay was approximately 0.7 mils thick and the titanium enriched diffusion zone 0.8 mils on both columbium base substrates. Siliconizing then produced Cr-Ti-Si coatings which were 1.8-2.5 mils in thickness.

Cyclic oxidation testing at 1800 and 2500°F (in air) involved one cycle to room temperature each hour for 8 hours, followed by 16 hours of static exposure in each 24 hour period. At 2700°F the coupons were cycled to room temperature for observation once each hour until failure. The specimen support material at all temperatures was high purity Al_2O_3.

Only one coupon of the 40 tested at 1800°F failed within the test duration time of 120 hours (B-66 alloy - 52 hours). At 2500°F the maximum and average protective lives of the Cr-Ti-Si coatings on B-66 alloy were 168 and 112 hours, respectively. For D-43 alloy the analogous protective lives were approximately 20% less at 148 and 88 hours, respectively. For exposure at 2700°F the maximum and average protective lives were 12 and 6.9 hours for B-66 alloy, and 12 and 8.4 hours for D-43 alloy, respectively. For the 2500 and 2700°F test temperatures the average protective lives of these coatings were approximately 25% higher than those previously determined in the reliability study of the Cr-Ti-Si system, conducted under a previous contract (AF 33(657)-7396) [2]. In this current study the test termination time was relatively short for evaluating the coatings at 1800°F, however, the coatings displayed no tendency toward poor low temperature behavior.

4.2 Cr-Ti-Si Coating Formation Analysis

The objective of the coating formation analysis was to characterize the basic factors influencing the formation of the Cr-Ti-Si coating on columbium. This involved the determination of coating formation rates, the delineation of composition profiles across the many stratified layers of the coating and phase identification. Metallographic analyses, electron micro-probe analyses, electron microscopy and X-ray diffraction studies were employed in this effort, and these findings are presented in the following subsections.

4.2.1 Metallographic Analysis

Table 5 presents the metallographic results for the terminated Cr-Ti coating runs shown schematically in Figure 1. These coating thickness data are shown graphically in Figures 5 through 7, as a function of processing time at 2300°F.

TABLE 4

Cyclic Oxidation Results for Cr-Ti-Si Coatings on D-43 and B-66 Alloys in the Diameter x 18" High Retort[a]

Test Temperature °F	No. of Test Specimens	Protective Life - Hours					
		B-66			D-43		
		Max.	Min.	Av.	Max.	Min.	Av.
1800	20	> 120	52	> 120	> 120	> 120	> 120
2500	20	168	54	112	148	48	88
2700	10	12	3	6.9	12	1	8.4

(a) Processing Conditions

Pack	Activator	Cycle	Nominal System Pressure
60Cr-40Ti	1.0 w/o KF	4 Hrs. - 2000° F + 8 Hrs. - 2300° F	10^{-2} mm
Silicon	0.5 w/o KF	6 Hrs. - 2100° F	10^{-2} mm

18

TABLE 5

Metallographic Measurements for Cr-Ti Coatings Formed in the
7 1/2" Diameter x 18" High Retort

Coating Conditions[1] Time-hours	Temperature-°F	Retort Position[2]	Metallographic Measurements – Mils					
			Unalloyed Columbium		B-66		D-43	
			Overlay	Diffusion Zone	Overlay	Diffusion Zone	Overlay	Diffusion Zone
0	2300	Top	0	0	0	0	0	0
		Middle	0	0	0	0	0	0
3	2300	Top	0-0.1	0.2-0.3	0.05-0.1	0.2-0.3	0.05	0-0.1
		Middle	0.05-0.1	0.2-0.3	0.05-0.1	0.2-0.3	0.05	0-0.1
5	2300	Top	0.2-0.3	0.3-0.5	0.2-0.3	0.3-0.4	0.2-0.3	0.1-0.3
		Middle	0.2-0.4	0.3-0.6	0.2-0.3	0.3-0.4	0.2-0.4	0.2-0.3
8	2300	Top	0.3-0.4	0.4-0.6	0.3-0.4	0.4-0.6	0.4-0.6	0.3-0.5
		Middle	0.3-0.5	0.6-0.8	0.3-0.4	0.4-0.6	0.4-0.6	0.4-0.5
2/0	2000/2300	Top	0	0	0	0	0	0
		Middle	0	0	0	0	0	0
4/0	2000+/2300	Top	0-0.2	0	0-0.2	0	0	0-0.2
		Middle	0.02	0.05-0.1	0-0.2	0.05	0	0-0.2
4/3	2000+/2300	Top	0.1-0.2	3-0.5	0.1-0.2	0.3-0.5	0.1-0.2	0.3-0.4
		Middle	0.3-0.4	4-0.6	0.3-0.4	0.5-0.7	0.2-0.4	0.5-0.6
4/5	2000+/2300	Top	0.2-0.3	0.4-0.7	0.2-0.3	0.4-0.7	0.3-0.4	0.4-0.5
		Middle	0.2-0.4	0.6-0.8	0.3-0.5	0.5-0.7	0.3-0.5	0.5-0.7
4/8	2000+/2300	Top	0.4-0.5	0.5-0.7	0.4-0.5	0.5-0.7	0.4-0.6	0.5-0.6
		Middle	0.4-0.7	0.7-0.9	0.6-0.8	0.6-0.8	0.6-0.8	0.6-0.8

(1) All runs – 60Cr-40Ti prealloyed powder pack, nominal system pressure 10-2 mm
(2) Specimens placed at mid-radius pack position in retort top and middle levels

19
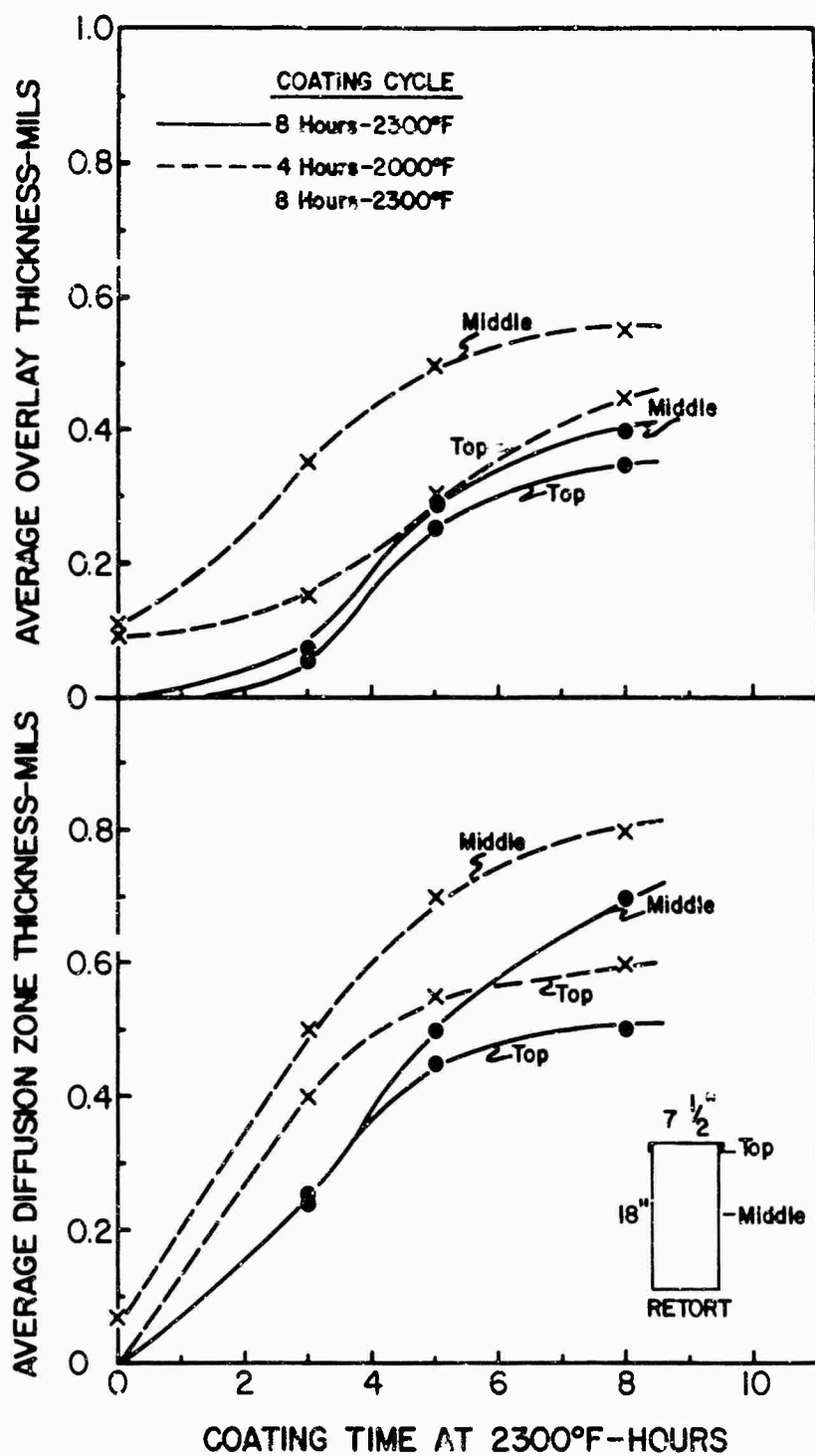
Figure 5   Cr-Ti Overlay and Diffusion Zone Thicknesses on Unalloyed
Columbium as a Function of Coating Time at 2300° F

20
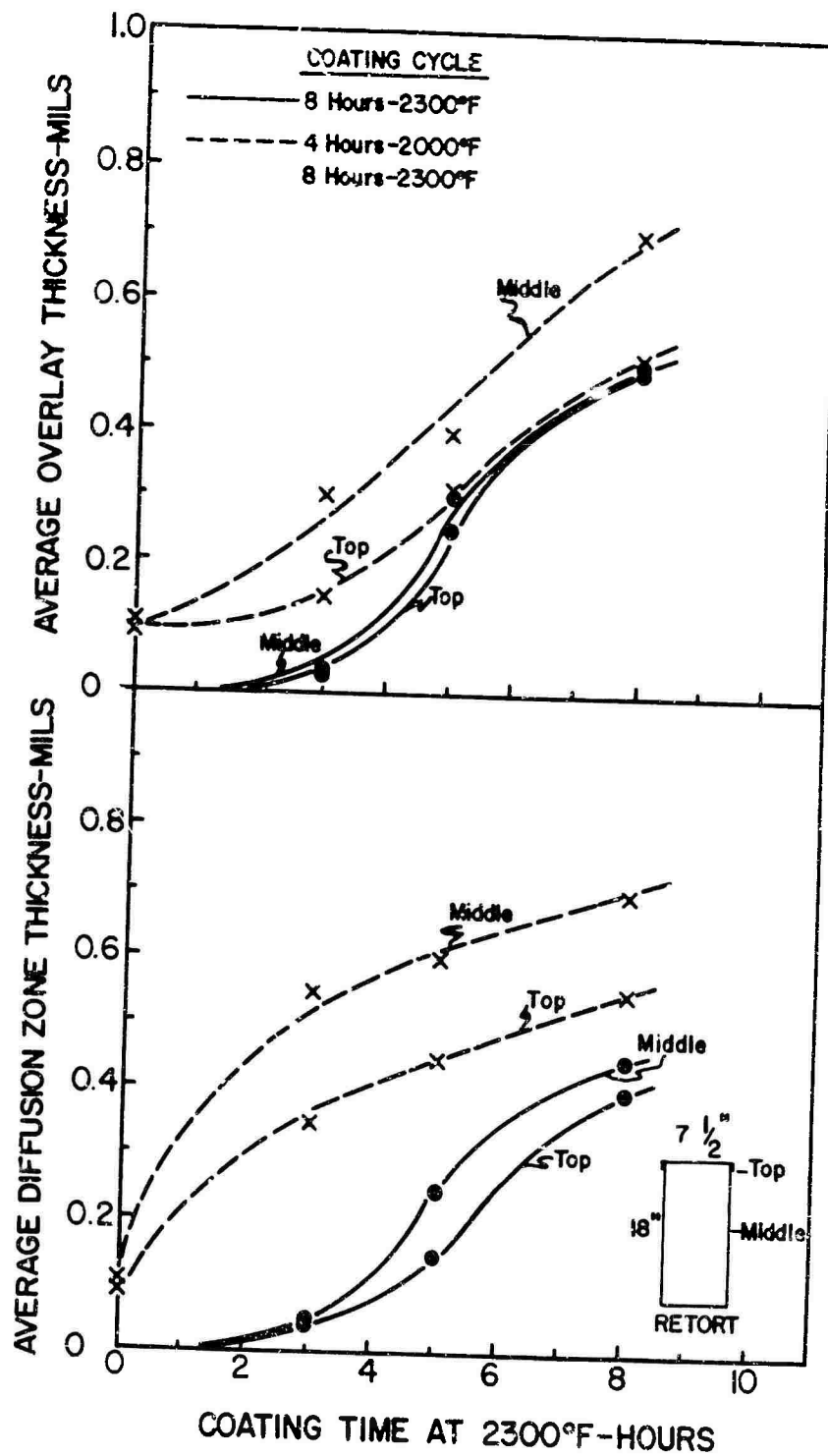
Figure 6   Cr-Ti Overlay and Diffusion Zone Thicknesses on D-43 Alloy
as a Function of Coating Time at 2300°F

21
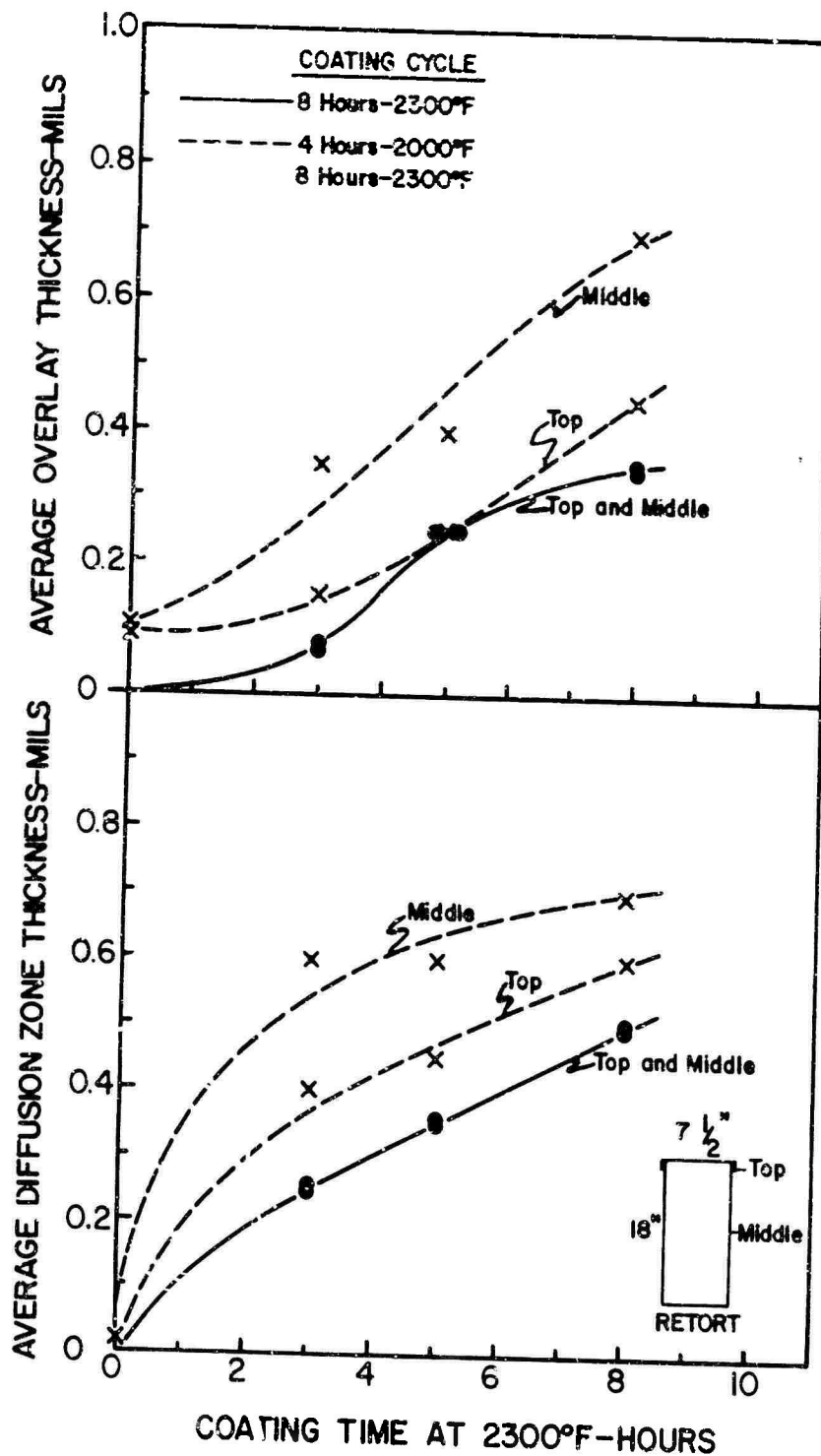
Figure 7 Cr-Ti Overlay and Diffusion Zone Thicknesses on B 66 Alloy as a Function of Coating Time at 2300°F

22

Direct heating of the furnace to 2300°F and immediately terminating the heating cycle produced no visible coating formation. Reference to Figure 2 shows that the internal pack temperature was still below 1000°F at this point, thus no coating formation would be expected. For coating times of 3 and 8 hours at 2300°F (furnace control temperature) simultaneous formation of the coating overlay and diffusion zone were observed, each increasing in thickness with increasing time. Again referring to Figure 2, the internal pack temperatures were only 2100 and 2200°F (top and middle positions respectively) after 3 hours at the control temperature. Even though in 5 hours the vertical mid-point position in the pack had reached 2300°F, the temperature at the top portion of the pack had not exceeded 2260°F. This lower temperature at the top retort level accounts for the generally thinner overlay and lesser depth of diffusion with coatings formed at this pack location.

Use of the intermediate hold treatment at 2000°F markedly reduced the horizontal temperature gradient in the retort, and increased by a factor of two the total time specimens in the pack experienced the 2300°F coating temperature. This is clearly shown by the greater coating overlay thicknesses and diffusion depths realized with the latter coating cycle. However, more variation in overlay thickness was observed between the top and middle retort levels for this cycle, than was experienced by direct heating to 2300°F. The intermediate hold treatment appeared to have slightly increased the temperature differential between the top and middle retort levels during the early part of the 8 hour 2300°F cycle, as compared to direct heating to the coating temperature. This lag in the time-temperature history in the retort top is evidenced in the thinner overlays and diffusion zones of coatings formed in this region.

An inflection is observed in the plot of coating thickness (overlay and diffusion zone) as a function of furnace time at 2300°F. This inflection occurred in all cases at approximately 5 hours, which was coincident with the cycle time at which the internal mid-radius pack temperature reached equilibrium. This inflection was either not observed or occurred at approximately 2 hours in the two-step (4 hour hold at 2000°F) thermal cycles. Essentially three factors were competing to establish the rate of formation of coatings during various stages of the process cycle: (1) the gradual but continuous temperature increase in the pack until equilibrium was reached late in the coating cycle, (2) the time dependent depletion of the activator or activated coating species from the metallic pack, and (3) the isothermal diffusion phenomenon. Temperature rise was obviously the controlling factor early in the cycle, and this rise produced a continuously increasing rate of coating formation until thermal equilibrium was attained. Thereafter, activator depletion and diffusion were the rate controlling factors, the latter of which contributed to a parabolic nature of the time-temperature curve in the later stages of the coating cycle.

On the basis of metallographic examination, it appears that the use of the intermediate hold treatment served only to increase the amount of time during which the specimens were at the coating temperature, thereby increasing the coating thickness. No obvious benefit was derived toward the objective of increasing titanium diffusion in the substrate during the low temperature hold treatment.

Figure 8 shows photomicrographs comparing the Cr-Ti coatings on the three substrate materials. The salient difference in these microstructures is the presence of a dark secondary phase in the overlay coating on D-43 alloy, and the absence of this precipitate in the coatings on unalloyed columbium and B-66 alloy. These microstructures will be discussed further in connection with the electron microprobe analysis.

The metallographically measured coating thicknesses resulting from the prematurely terminated siliconizing runs are presented in Table 6 and shown in Figure 9. The relative locations of specimens in the retort (top and middle) were maintained for individual coupons throughout both the Cr-Ti and silicon coating cycles.

Terminating the heating cycle immediately upon reaching the 2100°F control temperature (0 hours) is observed to have resulted in the formation of 0.1-0.2 mils of Cr-Ti-Si coating. The furnace temperature probe indicated the internal pack temperatures were only 700°F (middle) and 1300°F (top) at this point in the cycle, and further increased (overshoot) only 300-400°F during the furnace cooling cycle. Virtually all of the Cr-Ti overlay was alloyed with silicon after 2 hours at the control temperature.

It is shown in Figure 9 that during the early stages of the coating cycle slightly thicker Cr-Ti-Si coatings were formed on coupons located in the top of the silicon pack. This trend was then reversed after approximately 4 hours at 2100°F, which consistently reflects the relative time temperature histories at these two internal pack locations. It should be noted that the original Cr-Ti overlay comprises 25-40% of the Cr-Ti-Si coatings formed during the 2 hour siliconizing cycle, whereas the analogous percentage is considerably less after the 4 and 6 hours siliconizing treatments. Figure 10 is a series of photomicrographs showing four stages involved in the 6 hour siliconizing treatment of Cr-Ti coated D-43 alloy. Additional photomicrographs of the Cr-Ti-Si coatings on all three columbium materials will be shown in conjunction with the presentation of the electron microprobe data.

4.2.2 <u>Electron Microprobe Analysis</u>

The electron microprobe analysis of the Cr-Ti-Si coating system was performed for TRW by Advanced Metals Research Corporation (AMR). Eight as-coated columbium alloy samples were analyzed by AMR, and a description of these specimens is given in Table 7. D-43 alloy was selected as the basic substrate material for this study, and a comparative EMP analysis
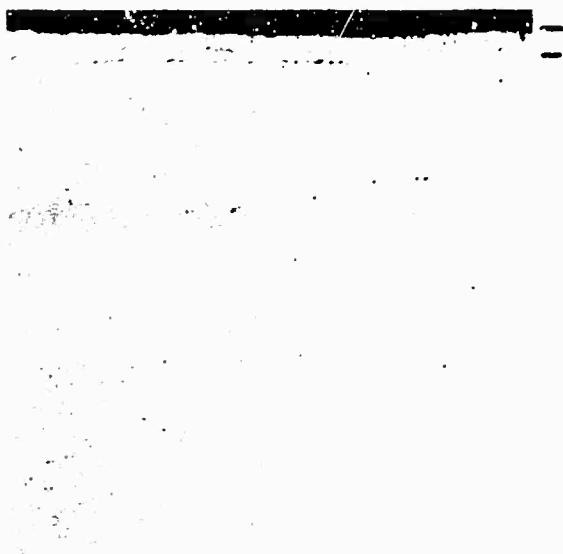
D-43 Alloy Substrate
Center Mid-Radius Pack Position
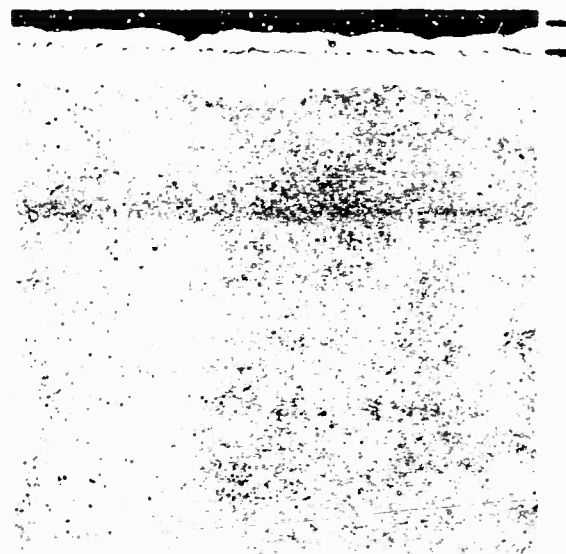
Unalloyed Columbium Substrate
Center Mid-Radius Pack Position
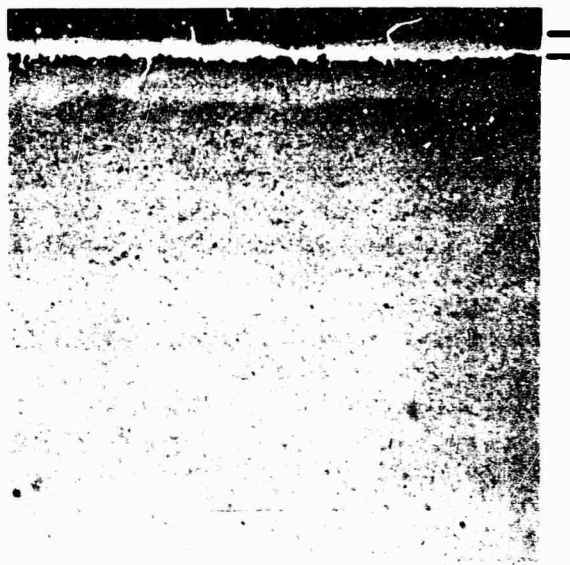
B-66 Alloy Substrate
Center Mid-Radius Pack Position

Figure 8   Cr-Ti Coatings Formed on Columbium Alloys Using 4 Hour - 2000°F + 8
Hour - 2300°F Coating Cycle, 60Cr-40Ti Pack, 7 1/2" Diameter x 18"
High Retort   250X

25

TABLE 6

Metallographic Results for Siliconizing Cr-Ti Coated
Columbium Alloys in 7 1/2" Diameter x 18" High Retort At
2100°F

Substrate	Pack Position	Cr-Ti-Si Overlay Thickness - Mils[a]			
		0 Hrs.[b]	2 Hrs.	4 Hrs.	6 Hrs.
Unalloyed Cb	Top	0.1 (0.2-0.3)	1.4-1.6 (0.2)	2.2-2.4	2.6
	Middle	0.1-0.2 (0.4-0.5)	1.0-1.2 (0.2)	1.8-2.2	2.8
B-66	Top	0.1-0.2 (0.3-0.5)	1.2-1.6	1.4-1.6	2.0-2.2
	Middle	0.1-0.2 (0.4-0.6)	1.0-1.2 (0.2)	1.8-2.4	2.2-2.6
D-43	Top	0.1-0.2 (0.3-0.5)	1.2-1.4	1.8	2.6
	Middle	0-0.1 (0.5-0.7)	(1.2-1.3) (0.1)	2.0-2.2	2.6-2.8

(a) Cr-Ti Coating Conditions
      8 hours - 2300°F
      60Cr-40Ti alloy
      System pressure - 10^{-2} mm

      Metallographic measurements - See Table 5

      Thickness of Cr-Ti overlay not alloyed with
      silicon shown in parenthesis

(b) Time at Coating Temperature - 2100°F

26
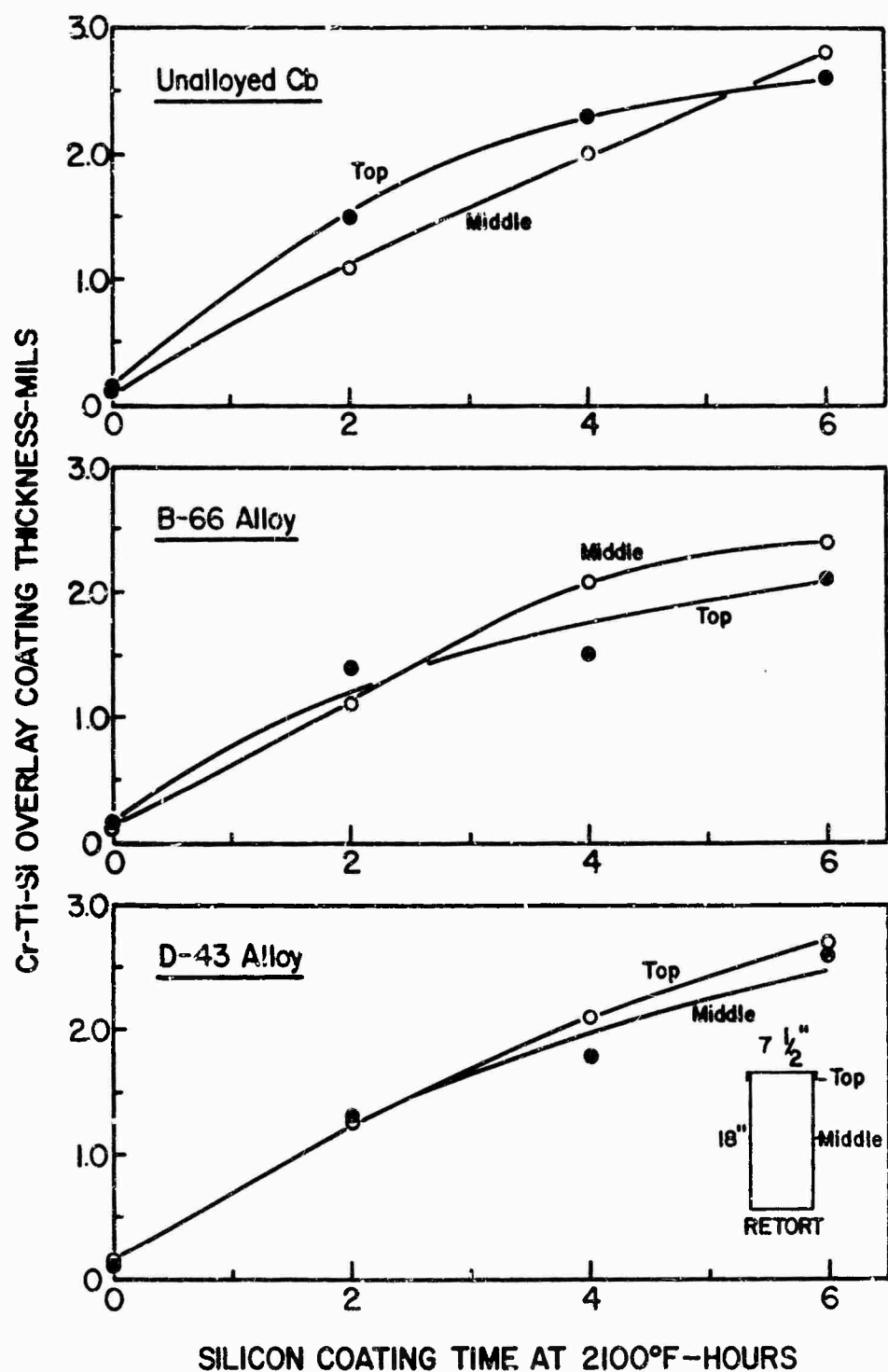
Figure 9 Cr-Ti-Si Overlay Thickness as a Function of Coating Time at 2100°F for Siliconizing of Three Cr-Ti Coated Substrates – Unalloyed Cb, B-66 and D-43 Alloys

O Hours   2100° F   2 Hours   2100° F
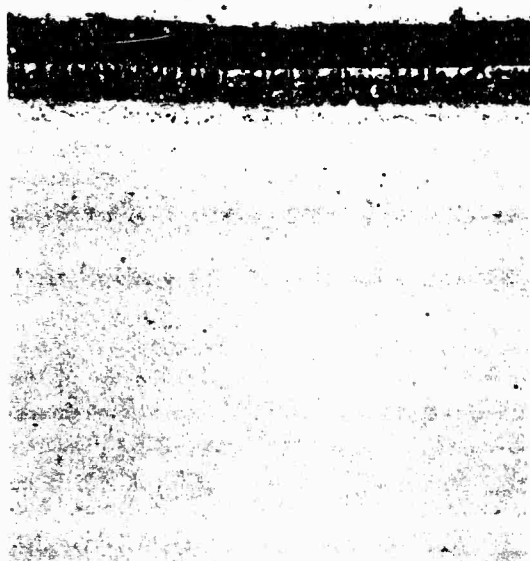
4 Hours   2100° F   6 Hours   2100° F

Figure 10   Photomicrographs Showing Various Time Stages in Siliconizing
Cr-Ti Coated D-43 Alloy – 7 1/2" Diameter x 18" High Retort –
Middle Position   250X

TABLE 7

Specimen Chemistry, Identification and Thermal History

Specimen	Substrate	Nominal Substrate Chemistry - w/o	Coating	Thermal Treatment Cr-Ti Cycle	Si Cycle
A	D-43(a)	Cb,10W,1Zr	Cr-Ti	5 hrs./2300°F	-
B	D-43	Cb,10W,1Zr	Cr-Ti	8 hrs./2300°F	-
C	D-43	Cb,10W,1Zr	Cr-Ti	4 hrs./2000°F + 8 hrs./2300°F	-
D	D-43	Cb,10W,1Zr	Cr-Ti-Si	8 hrs./2300°F	2 hrs./2100°F
E	D-43	Cb,10W,1Zr	Cr-Ti-Si	8 hrs./2300°F	6 hrs./2100°F
F	D-43	Cb,10W,1Zr	Cr-Ti-Si	4 hrs./2000°F + 8 hrs./2300°F	6 hrs./2100°F
G	B-66(b)	Cb,5Mo,5V,1Zr	Cr-Ti-Si	8 hrs./2300°F	6 hrs./2100°F
H	Cb	Cb	Cr-Ti-Si	8 hrs./2300°F	6 hrs./2100°F

(a) D-43 analysis 6.5 a/o W, 0.8 a/o Zr

(b) B-66 analysis 5.5 a/o Mo, 7.5 a/o V, 0.7 a/o Zr

was obtained with one as-Cr-Ti-Si coated coupon each of B-66 alloy and unalloyed columbium. Coupons A and B represent two time stages in the formation of the Cr-Ti alloy coating, and coupon C represents the influence of a 4 hour 2000° F hold treatment prior to the 8 hour 2300° F Cr-Ti coating cycle. Specimens D and E represent two time stages in the siliconizing cycle, and specimen F again involves the thermal hold treatment early in the Cr-Ti coating cycle. Specimens G and H are the B-66 alloy and unalloyed columbium specimens for comparison with D-43 alloy specimen E.

The element concentrations across these various coated samples were determined with an AMR electron beam microanalyzer. Two analyzing techniques were employed. X-ray spectrometers were aligned to record a pair of characteristic lines as each metallographically prepared specimen was slowly motor driven beneath the electron beam. The tranverse path was at an angle of 45° to the coating-substrate interface, and the traverse speed was 5 microns/minute. The available X-ray intensities were chart recorded as a function of beam position, thereby providing intensity profiles for each coating and substrate element. Point analyses were subsequently performed in specific areas of interest, such as distinct layers in the coatings and discrete phases. A curved mica crystal focusing spectrometer employing a helium path and flow-proportional counter, and a curved LiF crystal focusing spectrometer employing a scintillation detector, simultaneously recorded pairs of characteristic X-ray lines.

The recorded X-ray intensities were corrected for background and compared with the intensities of pure element standards. The resulting intensity ratios were converted to concentrations utilizing experimentally established calibration curves.

Figures 11 through 13 and 15 through 19 are photomicrographs of each of the specimens studied showing: (1) the element concentrations determined at various point locations across the coating and substrate microstructures and (2) the path of the EMP analysis. The values given at each location were obtained either by point analysis or by linear extrapolation of the element intensity profiles through the points of interest. The probe data is presented in this form rather than as concentration-penetration profiles because of the analytical technique employed. In continuously traversing a multi-phase material such as the Cr-Ti-Si coating, the electron beam is both passing through and overlapping many areas of distinctly differing composition. The characteristic X-ray intensities rise and fall depending on the combining elements, owing to variations in absorption, secondary fluorescence and atomic number effects. Therefore, the X-ray intensity record from the continuous traverse does not easily lend itself to the determination of a precise concentration profile across the coating microstructure. A series of discretely selected point analyses would better serve this purpose, and the subsequent probe analyses of these coatings were performed accordingly.

30

As shown in Figures 11 through 13, the Cr-Ti overlay coating on D-43 alloy is two phase, consisting of a bright matrix and a randomly distributed dark secondary phase. Areas near the coating surface and adjacent to the coating-substrate interface do not contain the dark phase. Beneath the overlay is a substrate diffusion zone, the depth of which is delineated by a "shading" effect in the photomicrograph, representing a differential in polishing behavior. In specimen A the overlay coating was only 8 microns in width, thus only a single chemistry is given for this area. Two or three point analyses in the overlay matrix are given for specimens B and C. Based on the chemistry of the overlay matrix, the Cr-Ti coating on D-43 alloy is an intermetallic compound of the form $(Cb,Ti) (Cr,W)_2$. X-ray diffraction data corroborating the identification of this compound are presented in Section 4.2.4. Columbium and titanium substitute in the chromide phase; with the concentration of columbium increasing and that of titanium decreasing as the substrate is approached. The dark secondary phase is titanium rich in comparison with matrix, and is most likely β titanium with chromium and columbium in solid solution.

In passing from the overlay into the diffusion zone a sharp increase in the concentration of titanium is observed. The titanium and chromium concentration gradients in the solid solution zone descend to zero just beyond the metallographically evident diffusion front. A chromium concentration of approximately 18 a/o was determined in the diffusion zone adjacent to the overlay-diffusion zone interface. Diffusion alloying of the columbium matrix with titanium apparently increased the solubility of the columbium for chromium, since less than 10 a/o chromium is soluble in pure columbium at room temperature[3].

The chemistries of all three Cr-Ti alloy coatings were quite similar, the essential difference being simply an increase in layer thickness with increasing coating time. Figure 14 is a plot showing the approximate element concentration profile of a Cr-Ti coating on D-43 alloy (specimen C). The profile represents a linear connection of the point chemistries given in Figure 13. Tungsten from the D-43 alloy was detected in significant concentrations throughout the overlay coating, whereas the zirconium concentration was essentially nil.

Figure 15 presents the microprobe results from a Cr-Ti-Si coating which is representative of an intermediate stage in the siliconizing cycle. The siliconizing time was 2 hours (2100°F); and it is evident from the photomicrograph that silicon had not entirely penetrated the original Cr-Ti alloy layer. The diffusion zone chemistry of specimen D is therefore essentially unaltered from that determined for specimen B, which is the original Cr-Ti coating.

A point analysis in the residual chromide phase evidenced approximately 8 a/o silicon in solid solution, substituting essentially for chromium. Remnants of the β Ti phase present in the original Cr-Ti alloy overlay are observed in the silicide microstructure, near the metallographically evident silicon diffusion front.

31

Element Concentration - Atomic Percent

Cb	W	Zr	Cr	Ti	Si	Source(a)
92.7	6.5	0.8	-	-	-	PA
76	6	0.1	6	12	-	EX
42	6	0.1	17	35	-	EX
15	2	0.05	62	21	-	Avg.

(a) Source: PA - Point Analysis
EX - Extrapolation
Avg. - Average

D-43 Substrate

Diffusion Zone 15μ

Overlay 8μ

Mag: 540X

A
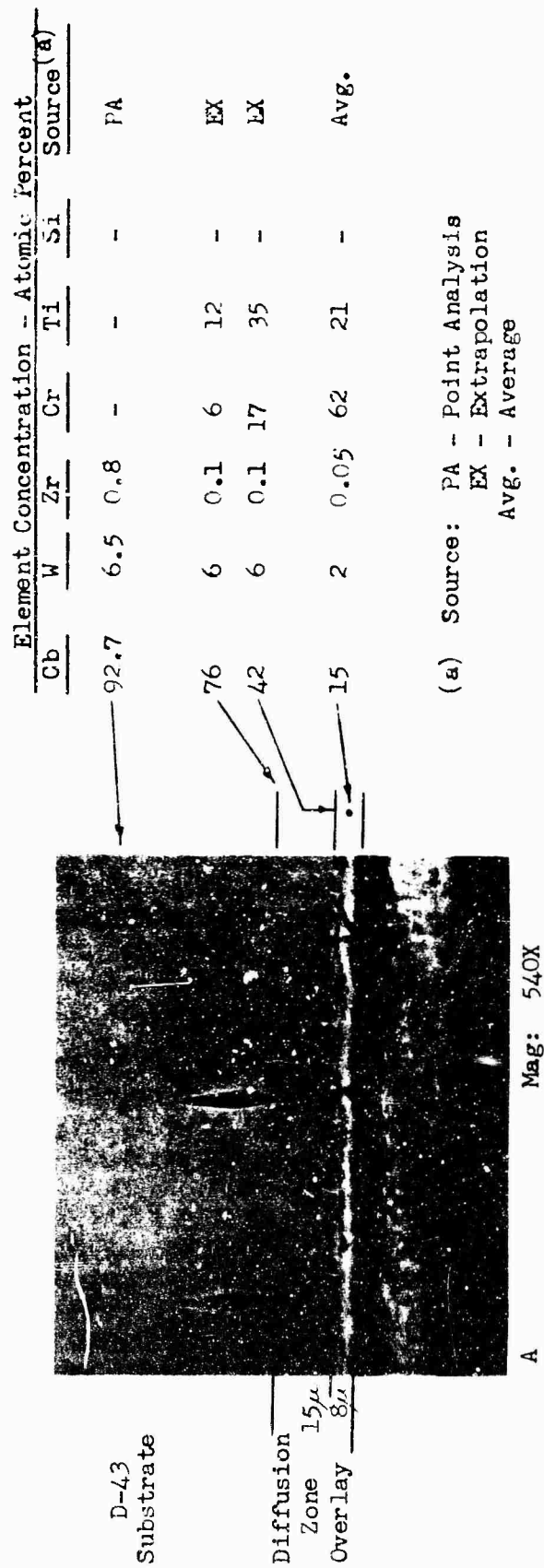
Figure 11 Photomicrograph and Microprobe Data for Cr-Ti Coated D-43 Alloy Coupon - Specimen A

	Element Concentration - Atomic Percent						
	Cb	W	Zr	Cr	Ti	Si	Source(a)
D-43 Substrate	92.7	6.5	0.8	-	-	-	PA
Diffusion Zone	83	7	0.2	6	4	-	EX
	42	7	0.2	18	33	-	EX
Overlay	18	3	0.2	64	15	-	PA(b)
	8	0.7	(d)	68	25	-	PA(c)

(a) Source: PA - Point Analysis
              EX - Extrapolation

(b) 5μ from Interface

(c) 5μ from Surface

(d) Zr < 0.05 a/o

Mag: 540X

B

23μ

18μ
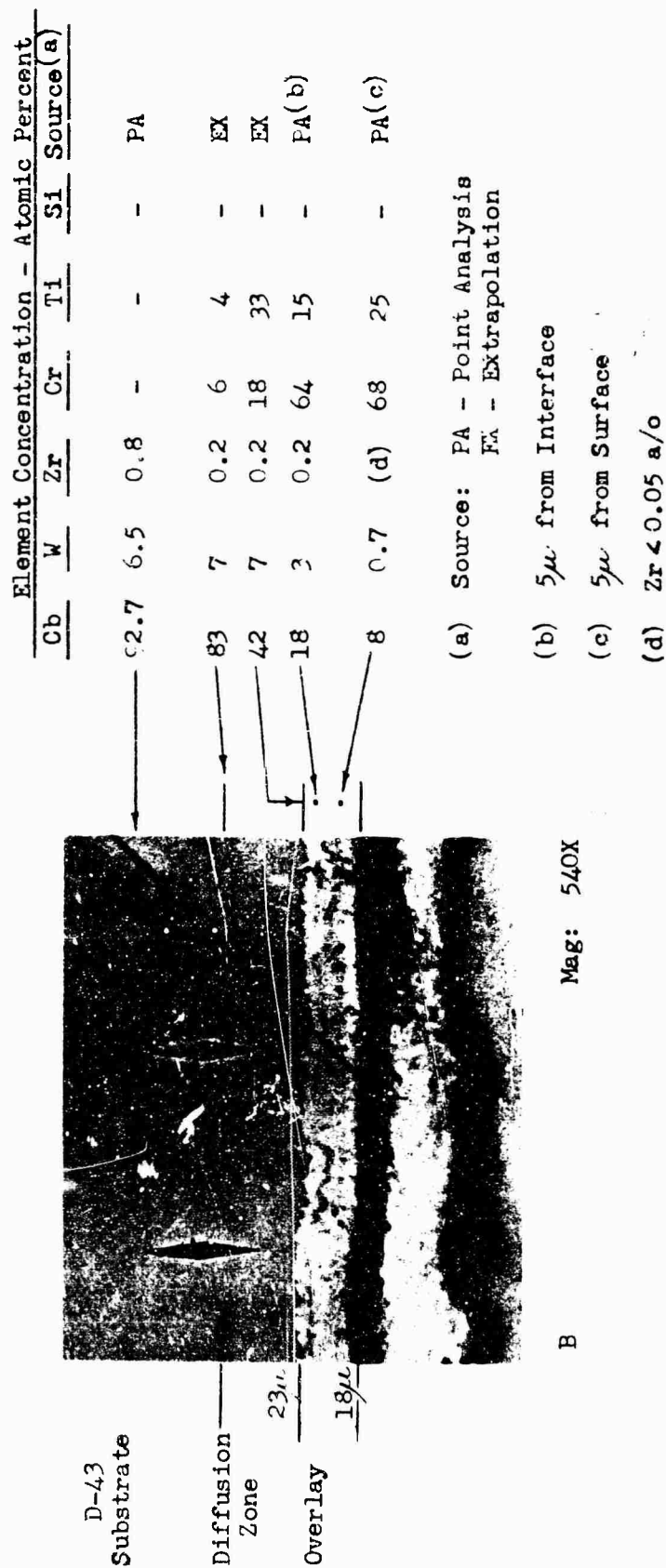
Figure 12 Photomicrograph and Microprobe Data for Cr-Ti Coated D-43 Alloy Coupon - Specimen B

	Element Concentration - Atomic Percent						
	Cb	W	Zr	Cr	Ti	Si	Source(a)
D-43 Substrate	92.7	6.5	0.8	-	-	-	PA
Diffusion Zone	87	6.4	0.5	3	3	-	EX
	45	6	0.2	17	32	-	EX
Overlay R	18	2	0.2	62	18	-	PA
S	10	1.5 (c)	(c)	24	65	-	PA(b)
T	9	1.0	-	67	23	:	PA

Mag: 540X

(a) Source: PA - Point Analysis
EX - Extrapolation

(b) In Dark Phase

(c) Zr < 0.05 a/o

Figure 13 Photomicrograph and Microprobe Data for Cr-Ti Coated D-43 Alloy Coupon - Specimen C

34
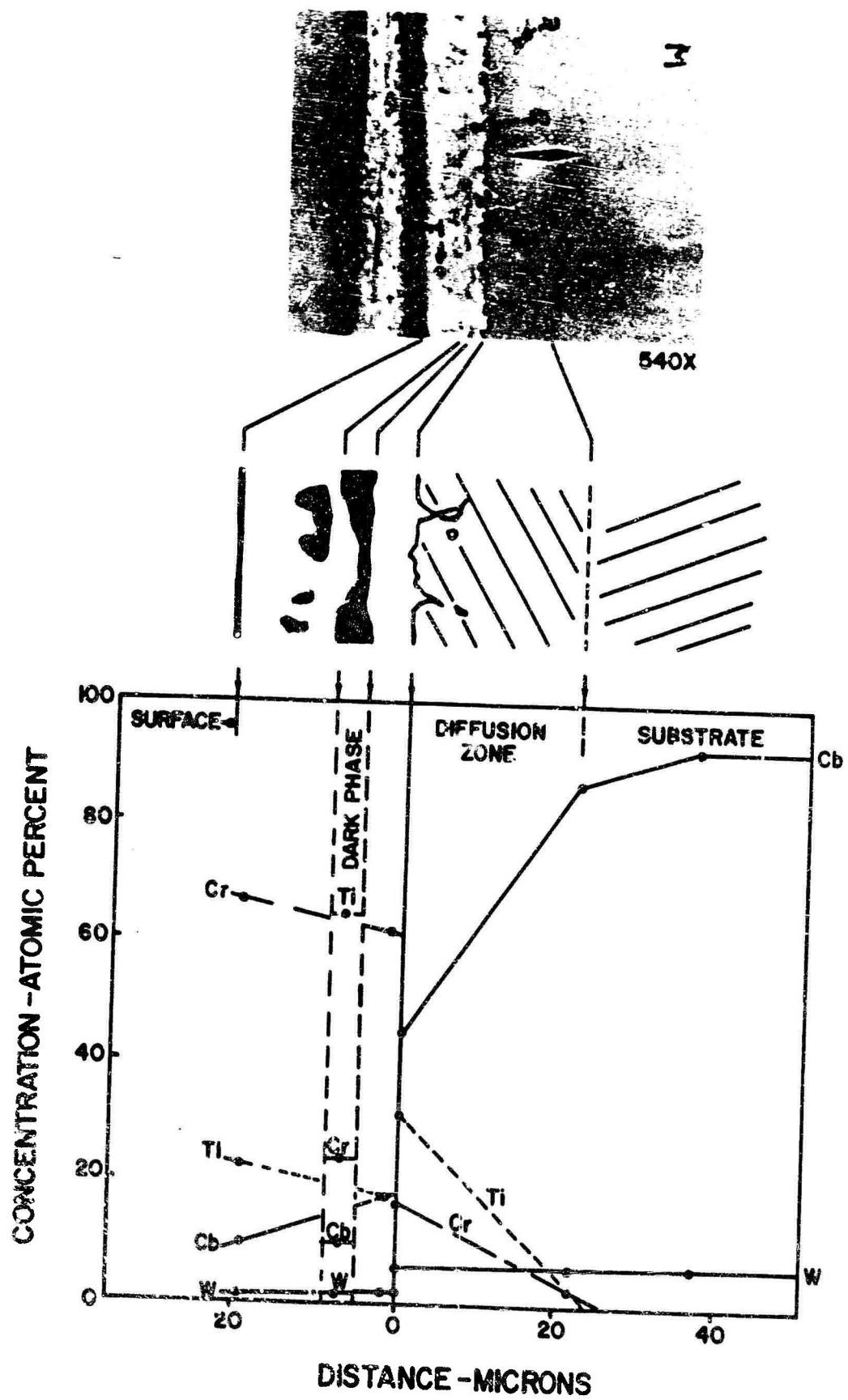
Figure 14 Concentration Profile for Cr-Ti Coated D-43 Alloy - Specimen C

35

	Element Concentration - Atomic Percent						
	Cb	W	Zr	Cr	Ti	Si	Source(a)
D-43 Substrate	92.7	6.5	0.8	-	-	-	PA
	90	7	0.2	2	1	-	EX
Diffusion Zone 18μ	45	7	0.1	15	33	-	EX
Residual Cr-Ti Alloy	21	5	0.05	52	14	8	PA
Silicide 35μ	5	0.7	-(b)	17	11	66	PA(c)
	4	0.5	-	19	9	67	PA

Mag: 540X

D

(a) Source: PA - Point Analysis
    EX - Extrapolation

(b) Zr < 0.05 a/o

(c) Point Analysis Between (3) and (4)
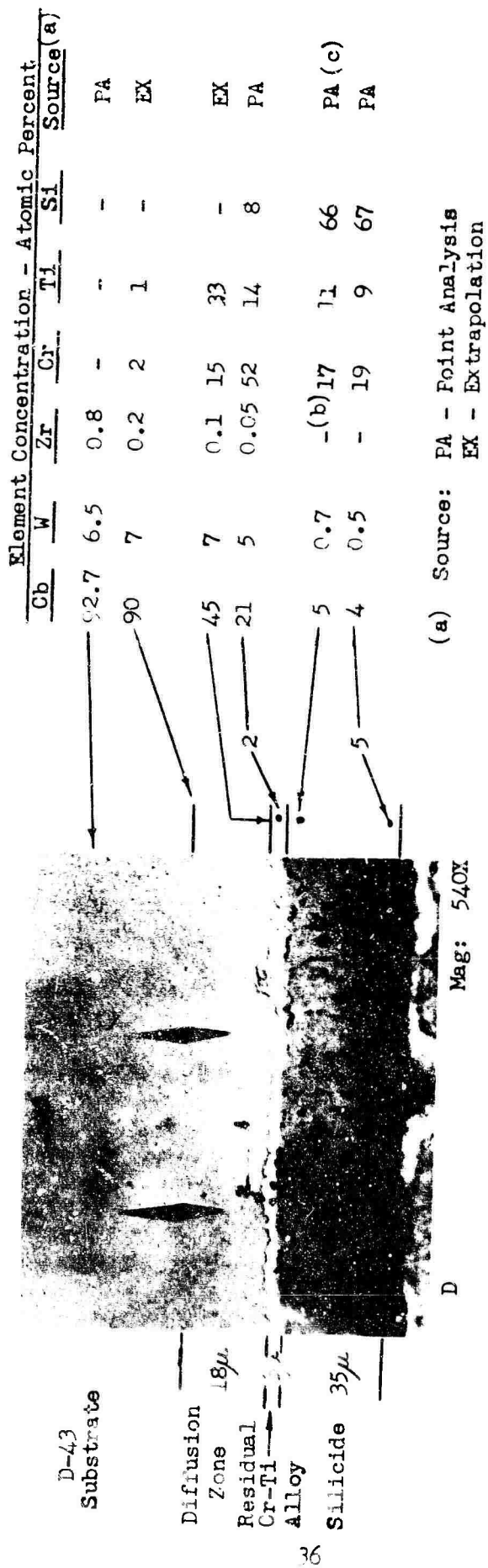
Figure 15 Photomicrograph and Microprobe Data for Cr-Ti-Si Coated D-43 Alloy - Specimen D

The concentrations of all elements are reasonably constant across the siliconized regions of the coating, and it is apparent that this region is a disilicide of the form $(Cr,Ti,Cb...)Si_2$. The concentrations of Cb, Cr and Ti in the disilicide constitute a dilution of these elements in the order of 1/3 to 1/2 their concentrations in the original Cr-Ti alloy layer.

Figures 16 (specimen E) and 17 (specimen F) show the microprobe results of Cr-Ti-Si coatings formed by siliconizing Cr-Ti coated coupons identical to specimens B and C, respectively. Figures 18 (specimen G) and 19 (specimen H) present similar data for Cr-Ti-Si coatings formed on B-66 alloy and unalloyed columbium. Specimens G and H were coated simultaneously with D-43 alloy specimen E. All of these coatings evidenced quite similar chemistries and will therefore be discussed as a group rather than individually.

The coatings consist of three distinct layers in the silicide overlay and a fourth region in the substrate which is the vestiges of the original titanium and chromium enriched diffusion zone. Summaries of the element concentrations in these various regions of the four specimens are tabulated in Tables 8 and 9 for ease of comparison. Figure 20 presents a schematic of the Cr-Ti-Si coating and a graphical representation of the concentration profiles across specimen F. The diffusion zone chemistries represent the element concentrations at the overlay-diffusion zone interface, obtained by extrapolation of the X-ray intensity profiles. One observation is of particular interest. Significant quantities of chromium and titanium are dissolved in the columbium substrate of all four specimens, however, the concentrations of these elements in unalloyed columbium are less than one-half the corresponding concentrations in the two columbium alloys. The Cr-Ti-Si coatings formed on unalloyed columbium were thicker than those formed on either of the columbium alloys, suggesting an attendant deeper penetration of silicon into the diffusion zone during siliconizing.

A narrow zone 3-5 microns in width is evident in the coatings adjacent to the substrate diffusion zone. This layer is a columbium rich silicide containing chromium, titanium and original concentrations of the substrate alloying constituents W, Mo, and V. This band apparently formed at the expense of the original diffusion zone which was formed during the Cr-Ti coating cycle. Based on the chemistries determined for this region, the layer may be analogous to the compounds Cb_3Si_2, or Cb_5Si_3, which would be symbolized $(Cb,Ti)_3(Si,W,Cr)_2$ or $(Cb,Ti,Cr)_5(Si,W)_3$, respectively. The concentrations of chromium and titanium in this layer are less than the concentrations of these elements in the adjacent diffusion zone.

The remaining two zones of the coating, which comprise approximately 95% of the Cr-Ti-Si coating, are disilicides of the form $(Cr,Ti,Cb,W...)Si_2$. The lighter layer adjacent to the previously discussed lower silicide band also appears to have formed at the expense of the original substrate diffusion zone. The corrugated interface between this layer and the adjacent layer which extends to the coating surface, is similar to the Cr-Ti overlay-substrate interface evidenced in specimens A through D.

37

Element Concentration – Atomic Percent

Cb	W	Zr	Cr	Ti	Si	Source[a]
92.7	6.5	0.8	-	-	-	PA
92.7	6.5	0.8	-	-	-	EX
49	7	0.1	17	23	4	EX
39	7	(b)	12	15	26	PA
15	4	-	6	10	65	PA
11	4	-	14	6	65	PA
4	0.5	-	20	9	66	PA

D-43
Substrate

Diffusion
Zone 18µ

5µ

8µ

Silicide

37µ

Mag: 540X

(a) Source: PA – Point Analysis
             EX – Extrapolation

(b) Zr < 0.05 a/o
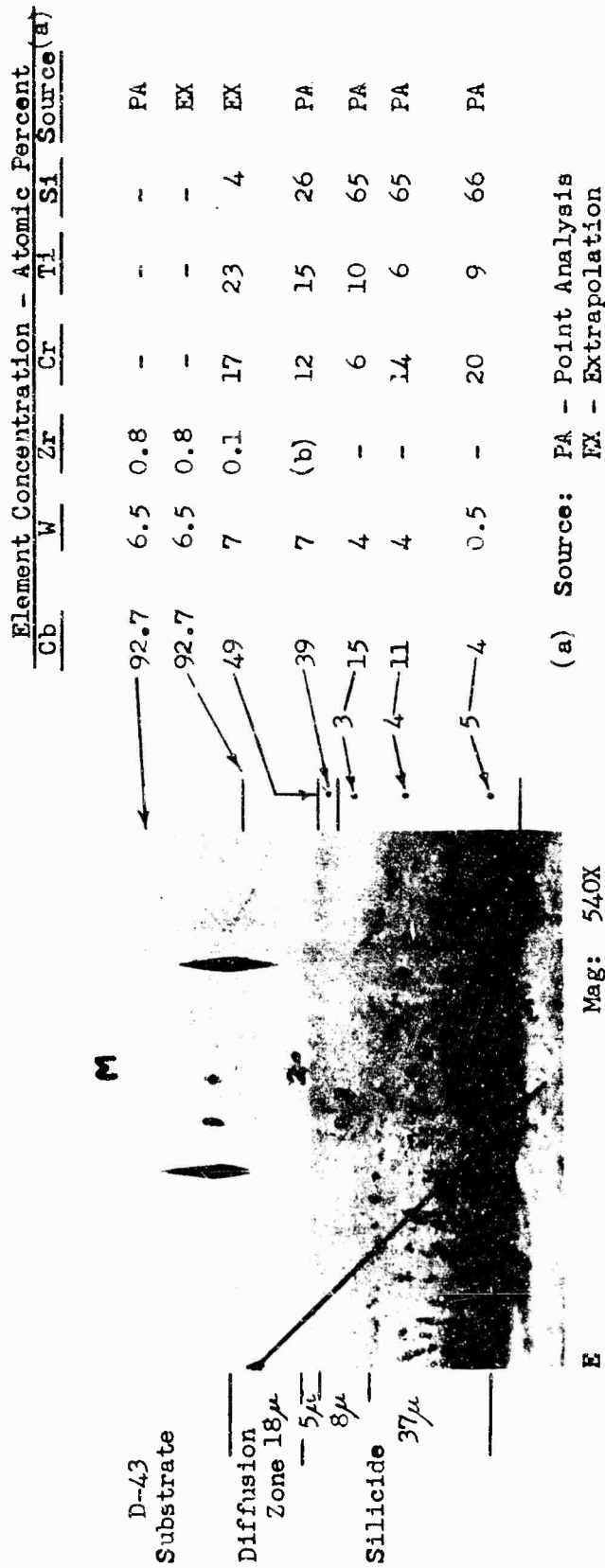
Figure 16 Photomicrograph and Microprobe Data for Cr-Ti-Si Coated D-43 Alloy – Specimen E

7359

Element Concentration – Atomic Percent						
Cb	W	Zr	Cr	Ti	Si	Source(a)
92.7	6.5	0.8	-	-	-	PA
90	6	0.8	2	1	-	EX
50	7	0.1	13	22	8	EX
45	8	0.05	12	13	22	PA
15	4	(b)	8	9	65	PA
11	3	-	15	6	65	PA
5	0.6	-	18	9	67	PA
0	0.6	-	21	11	67	PA

D-43 Substrate
Diffusion Zone 11μ 3μ 13μ
Silicide 43μ

Mag: 540X

(a) Source: PA – Point Analysis
EX – Extrapolation
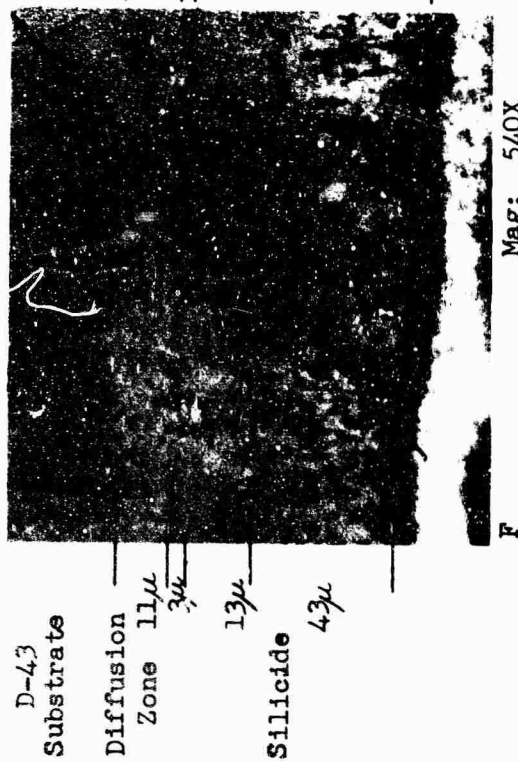
(b) Zr <0.05 a/o

Figure 17 Photomicrograph and Microprobe Data for Cr-Ti-Si Coated D-43 Alloy Coupon – Specimen F

39
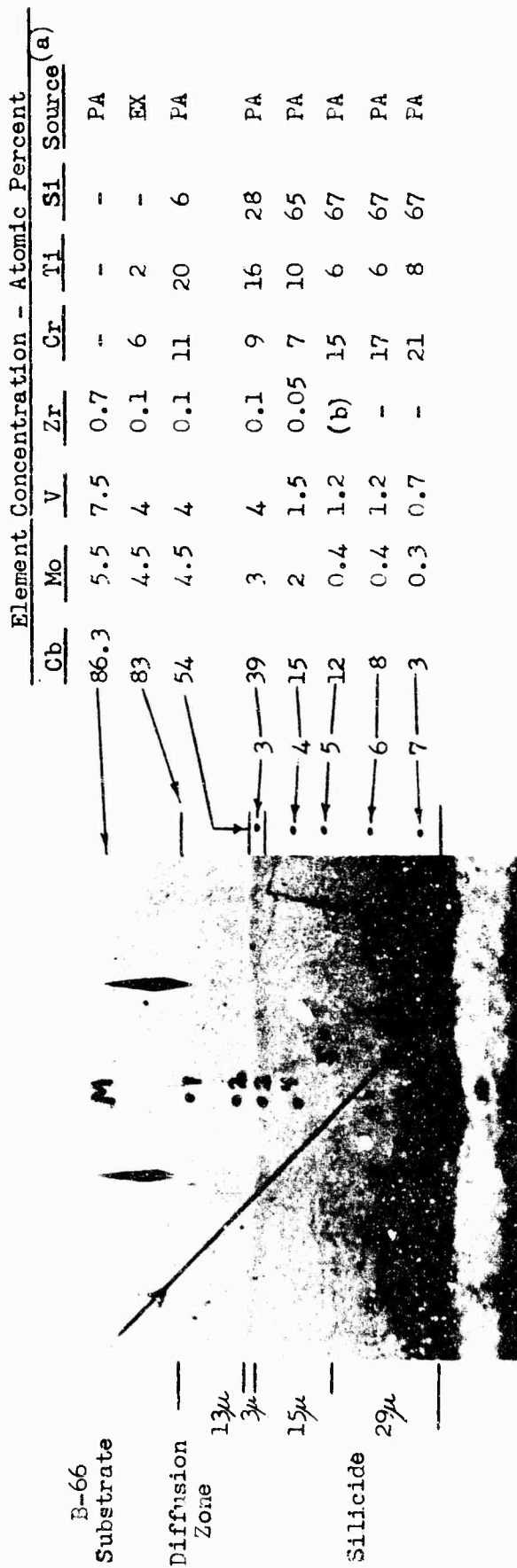
Figure 18 Photomicrograph and Microprobe Data for Cr-Ti-Si Coated B-66 Alloy Coupon - Specimen G

	Element Concentration - Atomic Percent							
	Cb	Mo	V	Zr	Cr	Ti	Si	Source[a]
B-66 Substrate	86.3	5.5	7.5	0.7	--	--	--	PA
	83	4.5	4	0.1	6	2	--	EX
Diffusion Zone	54	4.5	4	0.1	11	20	6	PA
	39	3	4	0.1	9	16	28	PA
	15	2	1.5	0.05	7	10	65	PA
Silicide	12	0.4	1.2	(b)	15	6	67	PA
	8	0.4	1.2	-	17	6	67	PA
	3	0.3	0.7	-	21	8	67	PA

(a) Source: PA - Point Analysis
EX - Extrapolation

(b) Zr < 0.05 a/o

Mag: 540X

G

40

7363

Element Concentration – Atomic Percent

Cb	Cr	Ti	Si	Source(a)
100	–	–	–	–
95	1	4	–	EX
84	11	5	–	EX
45	4	9	42	
18	6	11	65	PA
14	14	6	67	PA
7	19	6	67	EX

(a) Source: PA – Point Analysis
    EX – Extrapolation

Cb Substrate

Diffusion Zone 7μ 2μ 23μ

Silicide 43μ

Mag: 540X

H

Figure 19 Photomicrograph and Microprobe Data for Cr-Ti-Si Coated Unalloyed Columbium Coupon – Specimen H

TABLE 8

Comparison of Chemistries in Various
Regions of Specimens E through H

Concentrations - a/o

Specimen	Cb	W	Mo	V	Zr	Cr	Ti	Si
Diffusion Zone								
E	49	7	-	-	0.1	17	23	4
F	50	7	-	-	0.1	13	22	8
G	54	-	4.5	4.0	0.1	11	20	6
H	84	-	-	-	-	5	11	0
Substrate/Coating Interface Layer								
E(2/3)[a]	39	7	-	-	0.05	12	15	26
F(2)	45	8	-	-	0.05	12	13	22
G(3)	39	-	3	4	0.1	9	16	28
H(1/3)	45	-	-	-	-	4	9	42

[a] Denotes location of point analysis, as shown in Figures 11-19

TABLE 9

Comparison of Chemistries in Various
Regions of Specimens E through H

Specimen	Cb	W	Mo	V	Zr	Cr	Ti	Si
			Cb Rich Disilicide Layer					
E(3)	15	4	-	-	(a)	6	10	65
F(3)	15	4	-	-	(a)	8	9	65
G(4)	15	-	2	1.5	0.05	7	10	65
H(2)	18	-	-	-	-	6	11	65
			Cr-Ti Rich Disilicide Layer					
At Previous Layer								
E(4)	11	4	-	-	(a)	14	6	65
F(4)	11	3	-	-	(a)	15	6	65
G(5)	12	-	0.4	1.2	(a)	15	6	67
H(3)	14	-	-	-	-	14	6	67
At Surface								
E(5)	4	0.5	-	-	(a)	20	9	66
F	0	0.6	-	-	(a)	21	11	67
G(6)	3	-	0.4	0.7	(a)	21	8	67
H	7	-	-	-	-	19	6	67

(a) Zr Content <0.05 a/o
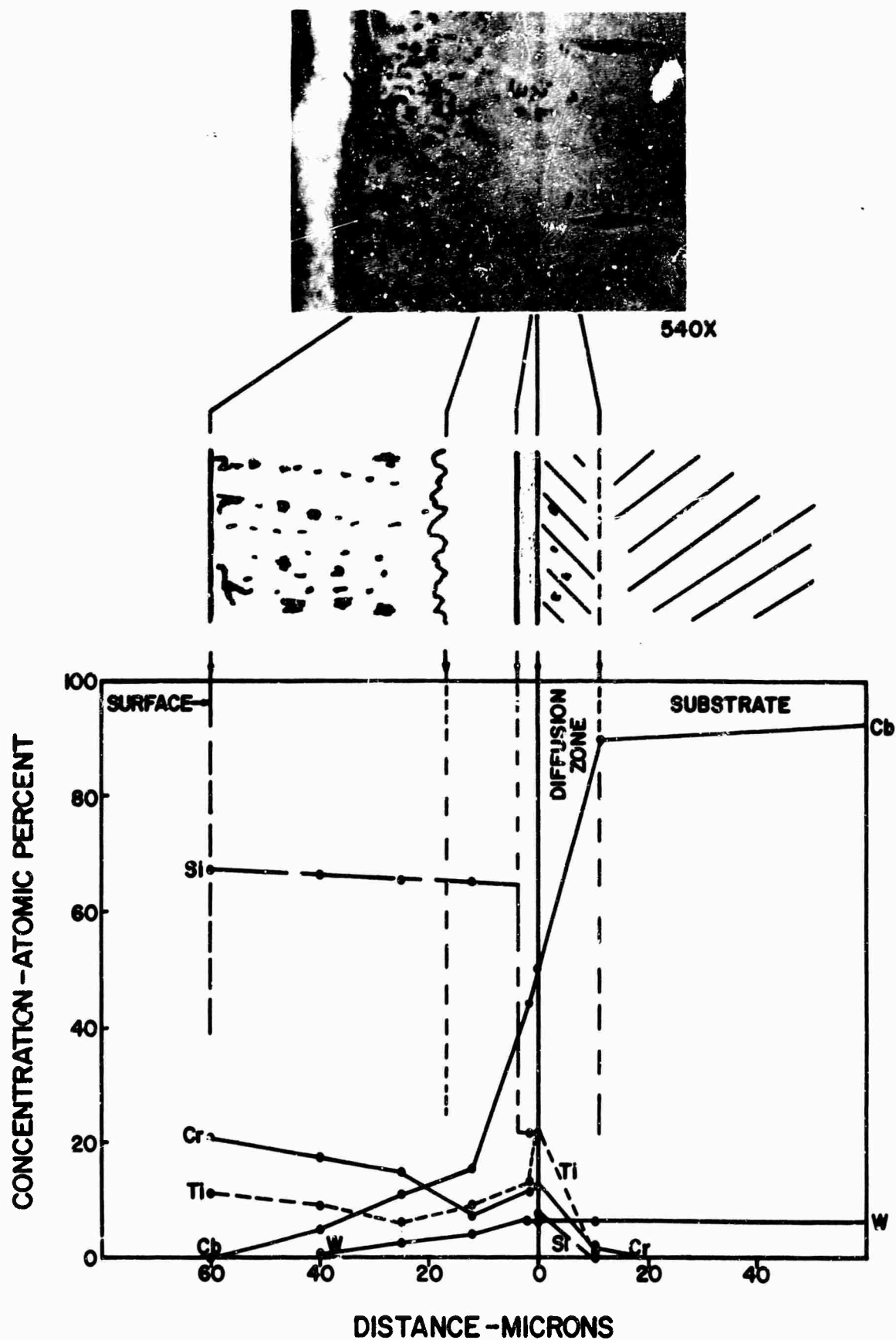
Figure 20   Concentration Profile for Cr-Ti-Si Coated D-43 Alloy -
              Specimen F

44

Also, this light etching layer was not observed in specimen D, in which case the original Cr-Ti alloy was not entirely penetrated by diffusing silicon. The composition of this layer is essentially the same in all four coatings, and is a region of minimum chromium concentration within the silicide.

The disilicide layer adjacent to the coating surface displayed approximately equivalent chemistries in all four coatings, with the exception of the absence of columbium near the surface of specimen F. The concentration of chromium in the Cr-Ti-Si coating is a maximum at the coating surface. This region of the coating formed by diffusion alloying silicon with the original Cr-Ti overlay. Chromium was the principal outward diffusing element during the siliconizing process. Figure 21 is a plot of element concentration profiles and a composite photomicrograph showing the redistribution of Cr, Ti and Cb during the siliconizing of Cr-Ti coated D-43 alloy. The concentration gradients indicate that the chromium and titanium diffused outward very rapidly to form the disilicide, whereas the columbium atoms were considerably less mobile. The titanium concentration essentially leveled out across the disilicide region, while the chromium increased in concentration towards the coating surface. The mobility of the chromium and titanium in solid solution in the columbium matrix was extremely low at the 2100°F siliconizing temperature, particularly in the absence of diffusing silicon.

The apparent location of the original Cr-Ti coating substrate interface in the Cr-Ti-Si coating was indicated previously, and additional evidence of this conclusion is shown in Figures 22 and 23. Figure 22 is a series of photomicrographs representing four time stages in the siliconizing of Cr-Ti coated D-43 alloy. The larger areas of the β Ti phase in the Cr-Ti alloy coating serve as markers during the siliconizing process, and the location of this phase is metallographically evident in the silicide after 2, 4 and 6 hours of siliconizing at 2100°F. Although it was not indicated previously, this region of the Cr-Ti-Si coatings did exhibit remnants of the titanium rich phase (β Ti) during the microprobe analysis. This was evidenced by titanium rich, chromium poor intensity spikes in the element distribution traverses.

A final confirmation of the interface shift is shown in Figure 23. Photomicrographs are shown of the transition zones from intentionally shielded to unshielded regions of Cr-Ti and Cr-Ti-Si coated D-43 coupons. The dark β Ti phase in the Cr-Ti coating appears continuous with a very thin coating layer on the shielded surface of the Cr-Ti coated coupon. This thin layer resulted from "throwing" of the Cr and Ti coating-vapors beneath the mechanically attached shield. The continuity of this thin layer with the dark precipitate in the chromide matrix suggests an approximate location of the original substrate surface in the Cr-Ti coating. After siliconizing, the β Ti phase is still evident, and can again be used to establish the approximate location of the original Cr-Ti alloy overlay in the as-formed silicide.

45
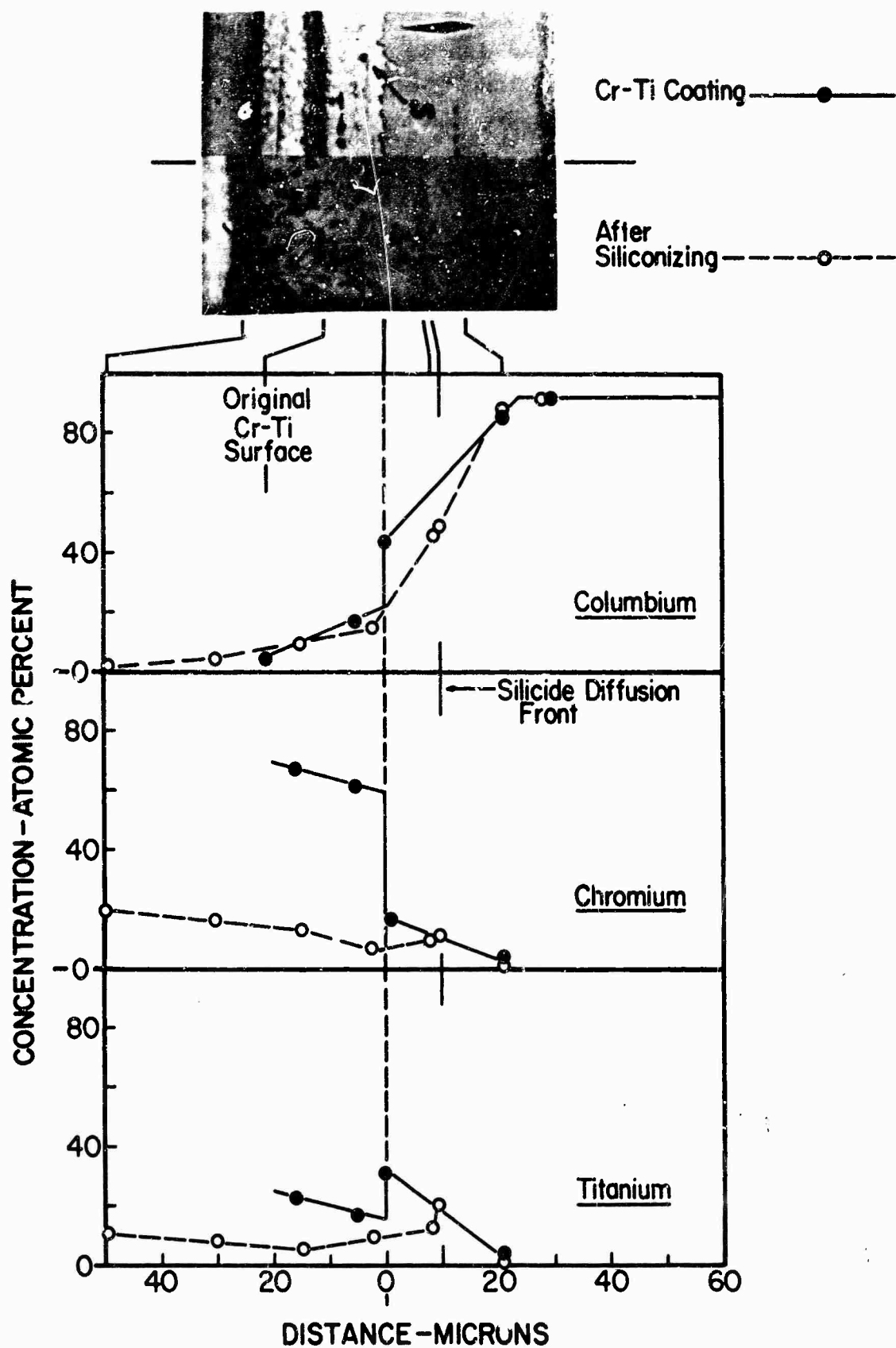
Figure 21 Concentration Profiles Showing Redistribution of Cr, Ti and Cb During Siliconizing of Cr-Ti Coated D-43 Alloy

46

βTi
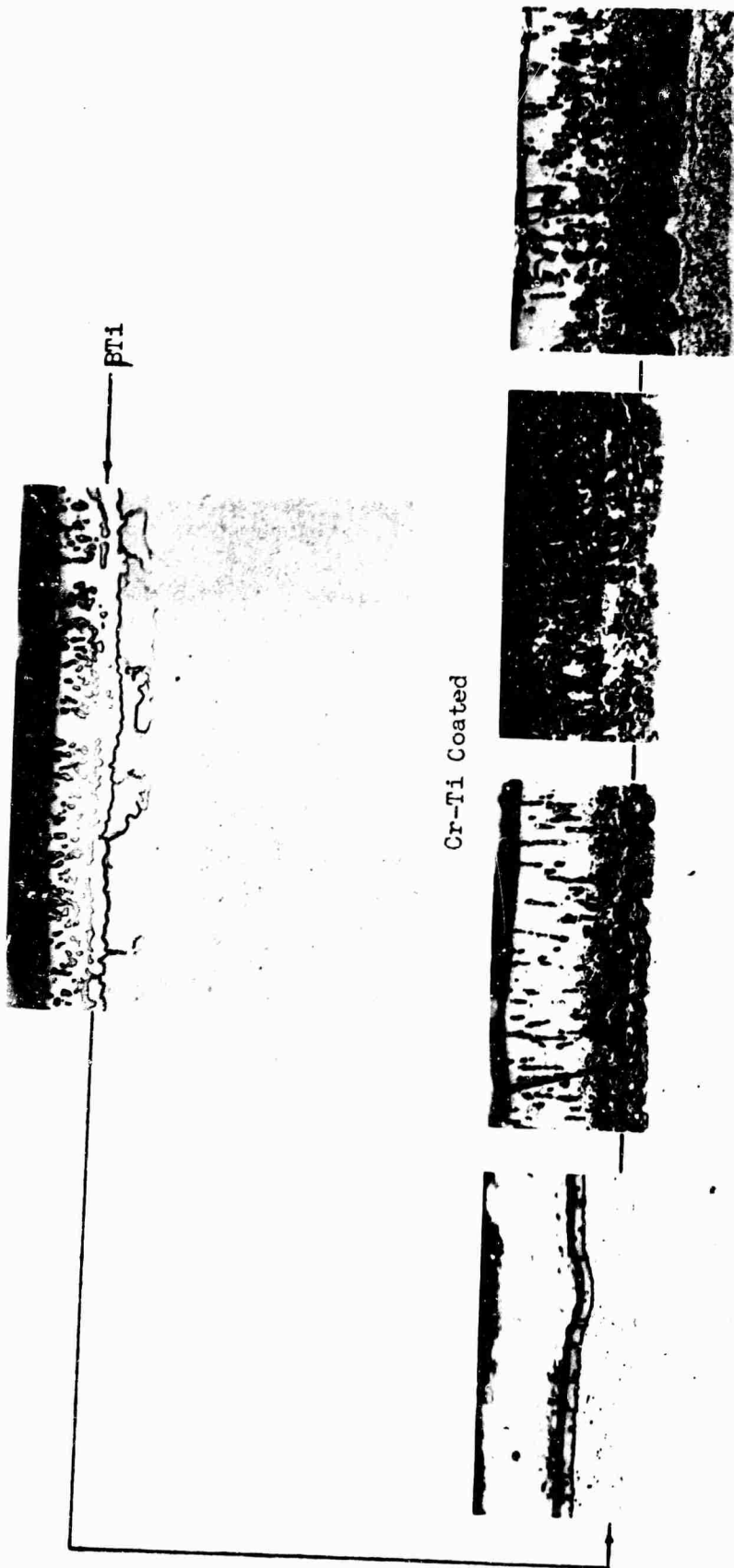
Cr-Ti Coated

0 Hours   2 Hours   4 Hours   6 Hours

Siliconizing - Furnace Time at 2000°F

Figure 22   Photomicrographs Showing Retention of βTi Phase During Siliconizing of Cr-Ti Coated
D-43 Alloy   500X

47

βTi →

Exposed
Surface

Shielded
Surface

Cr-Ti Coated D-43

Shielded
Surface

→ βTi

Exposed
Surface

Cr-Ti-Si Coated D-43

Figure 23   Photomicrographs of Cr-Ti and Cr-Ti-Si Coatings on D-43
Showing Transition from Shielded to Unshielded Surfaces
500X

48

Figure 24 is a reproduction of electron microprobe results obtained by Solar on Cr-Ti-Si coated B-66 alloy[4]. A comparison of this graph with the data in Figure 20 indicates quite similar compositional profiles, although the exact element concentrations are somewhat in variance. A higher titanium concentration in the diffusion zone is reported by Solar, and this could be the result of a lesser silicon penetration of the original Cr-Ti coating, as suggested by the photomicrograph.

Varying degrees of a second phase or inclusions are observed in the microstructures of the Cr-Ti-Si coatings, primarily near the external surface of the silicide. AMR performed a qualitative analysis of these inclusions by carefully positioning the electron beam on a typical particle and recording the complete spectral pattern. In addition to excitation of the surrounding matrix elements, characteristic X-ray lines of K, P and Ca were evident in the spectrum. The possible sources of these elements include the pack activators, impurities in the metallic pack materials, and handling impurities. The influence of these constituents on the protective capabilities of the Cr-Ti-Si was not investigated.

4.2.3 Electron Microscopy

An electron microscopy analysis was conducted with coupons coated simultaneously with those analyzed by the electron probe technique. Collodion replicas shadowed with chromium and backed with carbon were employed in this work. Electron micrographs are presented from several coated specimens, and reference is made to the analogous EMP specimens denoted A through H in Table 7.

In Figure 25 electron micrographs are shown of the interfacial zone in an as-Cr-Ti coated D-43 alloy specimen (specimen B), before and after siliconizing for two (2) hours at 2100°F (specimen D). A sharp interface is shown between the chromide Laves phase and the substrate diffusion zone. The β Ti phase evident in the Cr-Ti coating is undissolved after two (2) hours siliconizing, and is observed as distinct islands in the disilicide layer. The residual chromide phase is evident as an interposed layer between the diffusion zone and the advancing disilicide front.

Figure 26 is a composite electron micrograph showing approximately 50% of the coating cross section. The corrugated interface separating the two disilicide layers is coincident with the original Cr-Ti coating/substrate interface. The interfacial layer between the disilicide and the substrate diffusion zone was resolved into two distinct zones in the electron microscope. The electron microprobe analysis indicated the average chemistry of this region encompassed a possible solubility range of the lower disilicide and trisilicide phases. Goldschmidt and Brand indicate that α Cb_5Si_3 has considerable solubility for Cr, Cb and Si[5], and undoubtedly it also has an appreciable solubility for titanium. Increased chromium dissolution in the α phase has the effect of stabilizing the β Cb_5Si_3, to which Goldschmidt and Brand have assigned the representative forms $Cr_2Cb_3Si_3$ and $CrCb_2Si_2$. Based on
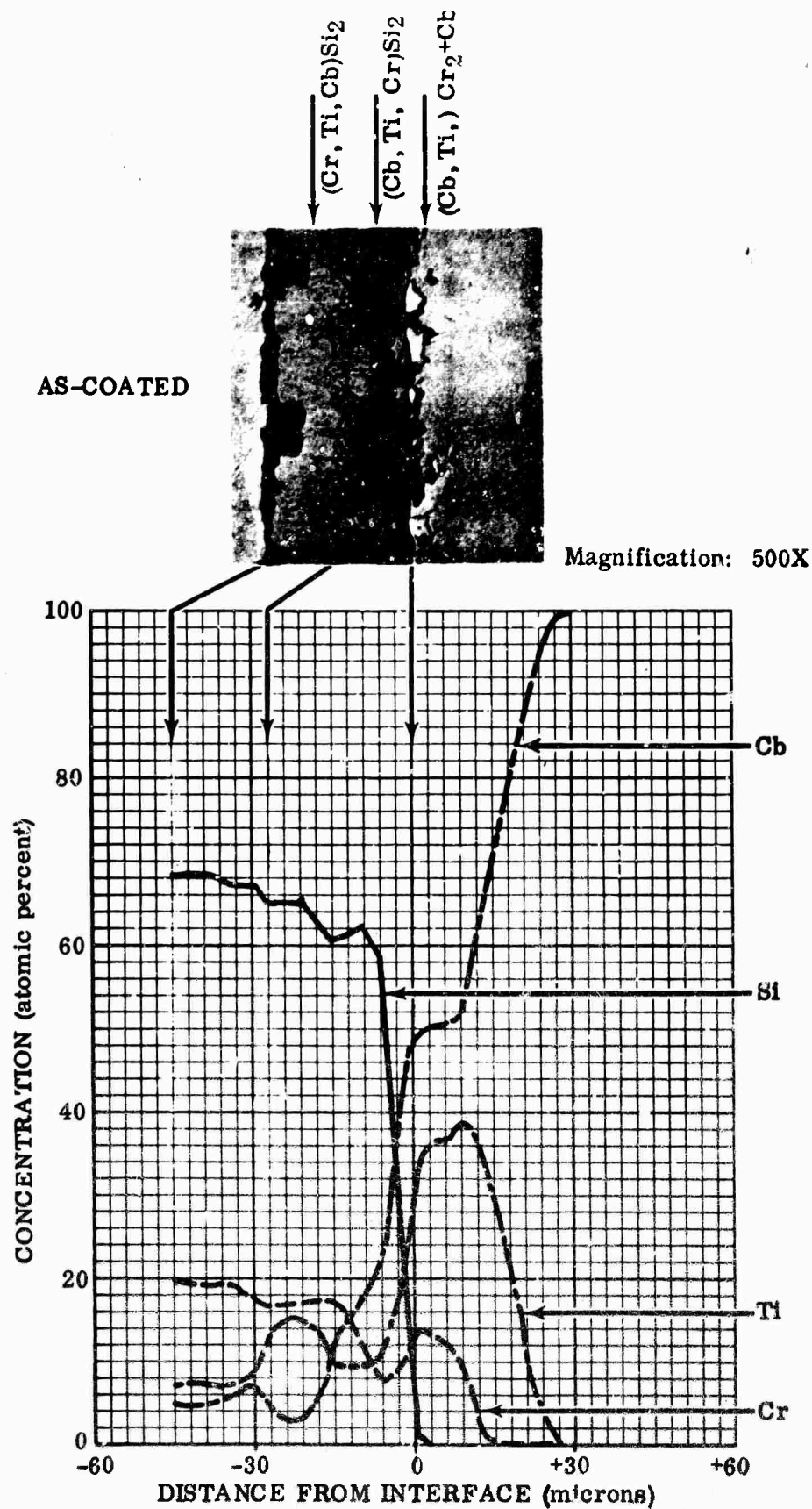
Figure 24 Concentration-Penetration Profile of Cr-Ti-Si Coating on B-66 Alloy - As Coated (4)

50
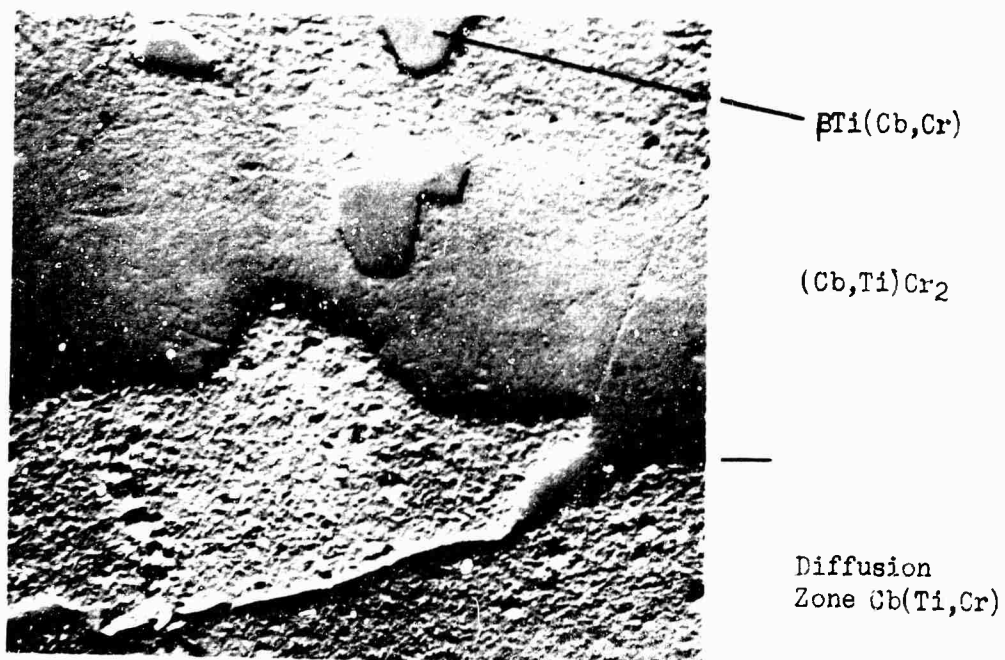
Cr-Ti Coated (B)   Mag: 8,000X
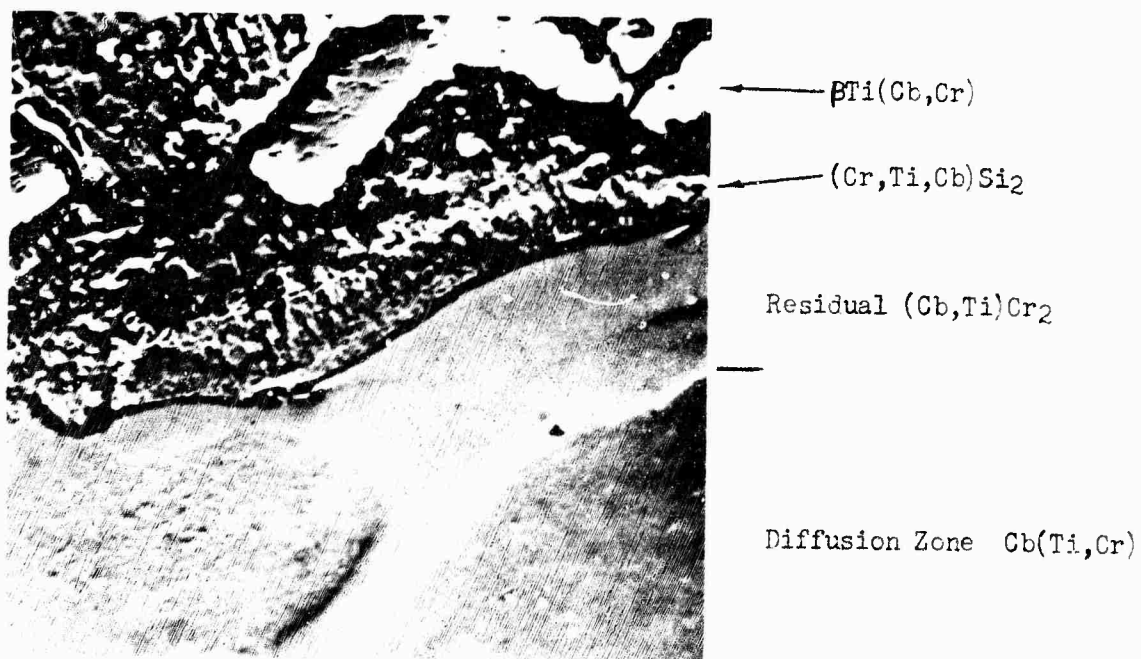
Cr-Ti-Si Coated (D)   Mag: 10,000X

Figure 25   Electron Micrographs of Cr-Ti and Cr-Ti-Si Coated D-43 Alloy

51

$(Cr,Ti,Cb)Si_2$

←—— Original
Cr-Ti Coating/Substrate
Interface

$(Cb,Ti,Cr)Si_2$

$(Cb,Cr,Ti)_3(Si,W)_2$

$(Cb,Cr,Ti)_5(Si,W)_3$

←——— Diffusion Zone Cb(Cr,Ti,Si)
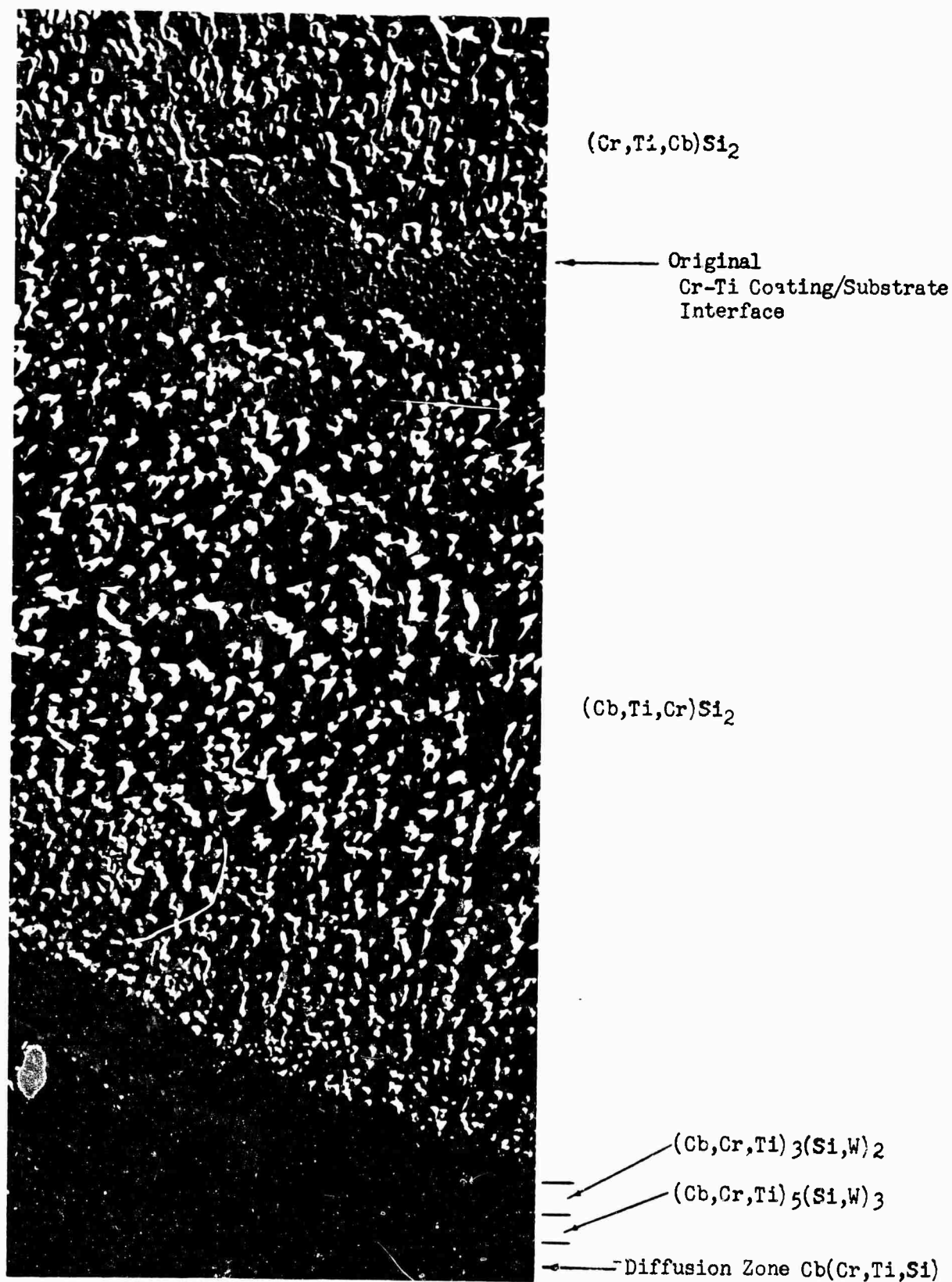
Cr-Ti-Si Coated (E)   Mag: 6,000X

Figure 26   Electron Micrograph of Cr-Ti-Si Coated D-43 Alloy - Specimen E

52

these prototypes, the very narrow layers are probably a form of the tri-silicide phase adjacent to the substrate and the lower disilicide phase adjacent to the coating. A higher magnification photograph of this interfacial region is shown in Figure 27; along with a lower magnification photograph of the overall Cr-Ti-Si coating which clearly shows the two disilicide regions (the inner columbium rich disilicide formed from the diffusion zone and the chromium and titanium rich disilicide formed from the Laves phase overlay).

Figure 28 is an electron micrograph from a Cr-Ti-Si coated D-43 alloy coupon (specimen F), showing particles in the disilicide region which are either the vestiges of the β titanium phase or a newly precipitated phase. The location of the original Cr-Ti/Cb interface is clearly indicated, including evidence of the original Laves phase formation in a substrate grain boundary.

4.2.4 X-Ray Diffraction Study

X-ray diffraction studies were conducted with both Cr-Ti and Cr-Ti-Si coated columbium alloy specimens, in the as-coated condition. Diffracto-meter patterns were obtained at various known levels through the coating. Successive layers were abraded from the surface in increments of 0.1-0.2 mil. Copper Kα radiation (λ = 1.54050) and a nickel filter were employed in this work. Two specimens were analyzed by this technique: (1) a Cr-Ti coated D-43 specimen analogous to EMP specimen B (Table 7) and (2) a Cr-Ti-Si coated D-43 coupon similar to specimen E.

The diffraction data from the Cr-Ti coating corroborated the EMP results, indicating the principal phase in the coating was a solid solution of the isomorphous Laves phases $CbCr_2$ and $TiCr_2$. DuWez and Martens reported $CbCr_2$ as fcc with a $MgCu_2$ type structure and a lattice parameter of a = 6.976 Å[6]. DuWez and Taylor identified $TiCr_2$ as also having a $MgCu_2$ type fcc structure with a = 6.943 Å[7]. The lattice parameter of the Laves phase across the Cr-Ti coating increased inward from the surface as shown in Figure 29. The parameter change corresponds to a transition from essentially $TiCr_2$ to $CbCr_2$, which agrees with the corresponding coating composition change as evidenced by the electron probe. Only two data points are shown for the element concentrations, and these values were determined by point analyses at 5 micron distances from the coating surface and internal interface. Each of the lattic parameter values represents an average of three determinations using the (222), (333) and (440) lines of the diffraction patterns.

Identification of the β titanium phase in the Cr-Ti coating was not conclusive, however, bcc lines corresponding to the d spacings of this phase were evident just beneath the coating surface. This phase evidenced a titanium concentration of 62 a/o in the EMP analysis. Both columbium and titanium possess bcc structures, with nearly identical lattice parameters (a = 3.30 Å) at room temperature. The sensitivity of the X-ray technique

53

Cr-Ti-Si Coated (E) Mag: 10,000X

$(Cb,Ti,Cr)Si_2$

$(Cb,Cr,Ti)_3(Si,W)_2$

$(Cb,Cr,Ti)_5(Si,W)_3$

Diffusion Zone

Cr-Ti-Si Coated (E) Mag: 2,600X

$(Cr,Ti,Cb)Si_2$

Original Cr-Ti Coating/Substrate Interface

$(Cb,Ti,Cr)Si_2$

Lower Silicides

Diffusion Zone
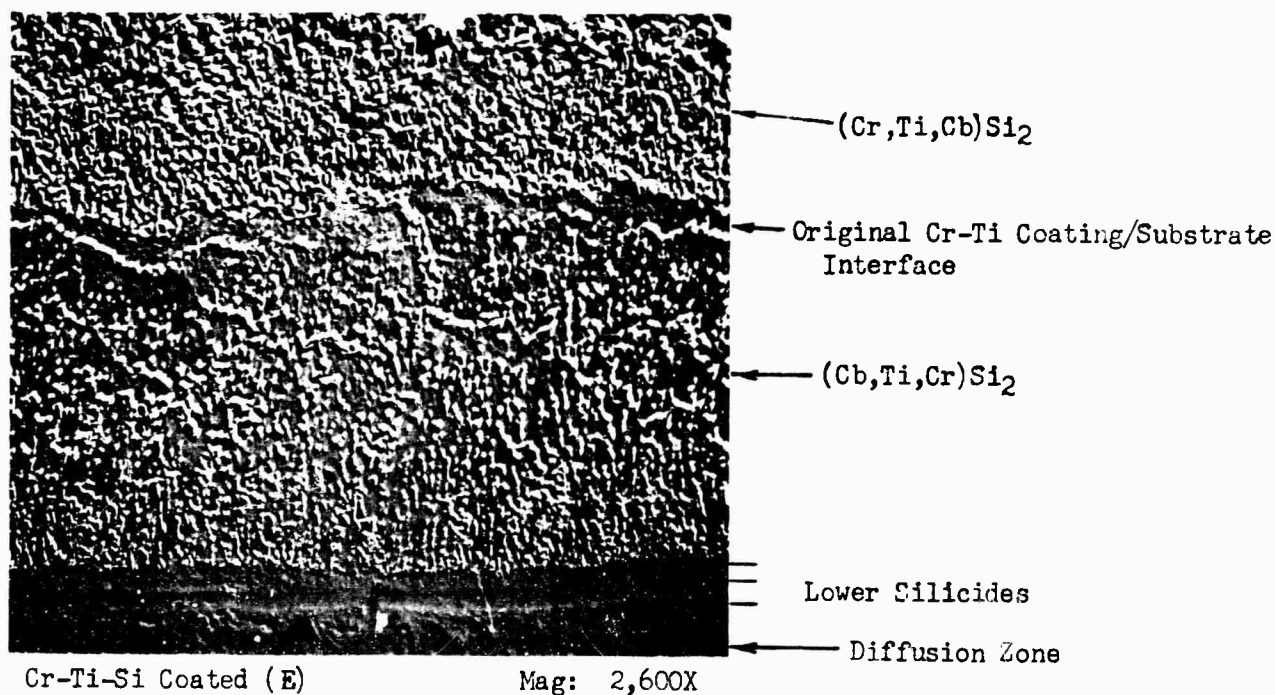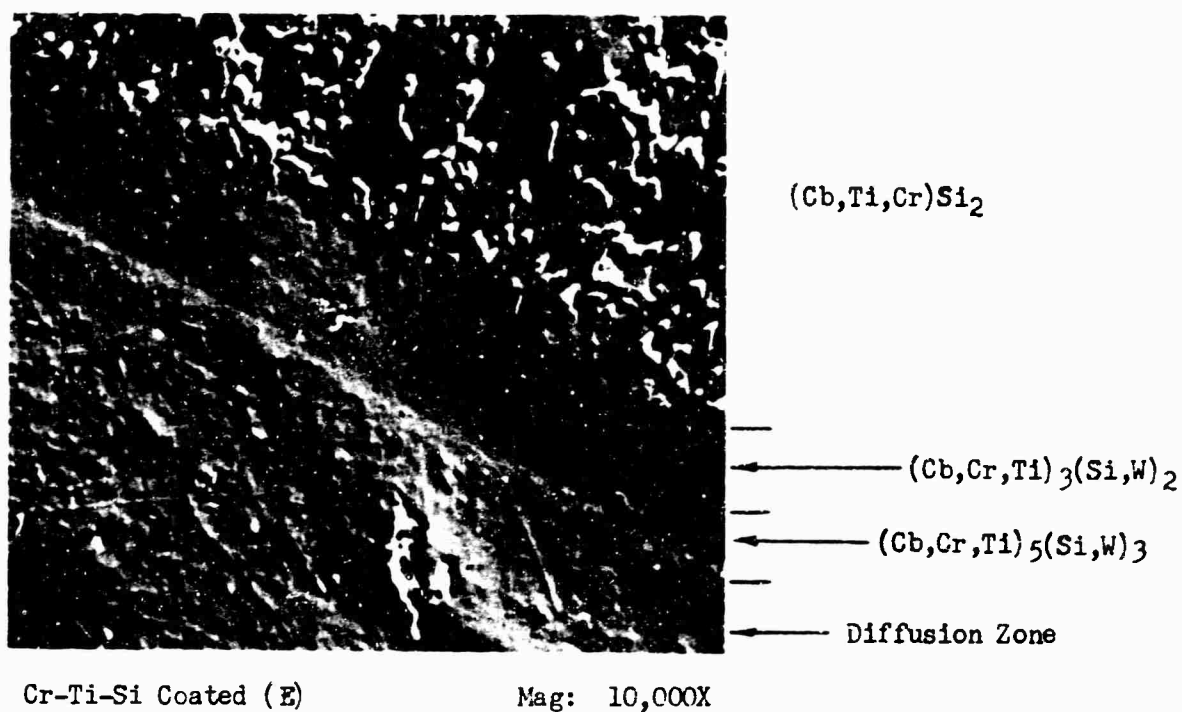
Figure 27 Electron Micrographs of Cr-Ti-Si Coated D-43 Alloy – Specimen E

Undissolved β Ti

Original
Cr-Ti
Coating/Substrate
Interface

— (Cb,Ti,Cr)Si$_2$

Vestiges of
Laves Phase in
Matrix Grain
Boundary

(Cb,Cr,Ti)$_3$(Si,W)$_2$

(Cb,Cr,Ti)$_5$(Si,W)$_3$

Diffusion Zone
Cb(Ti,Cr,Si)
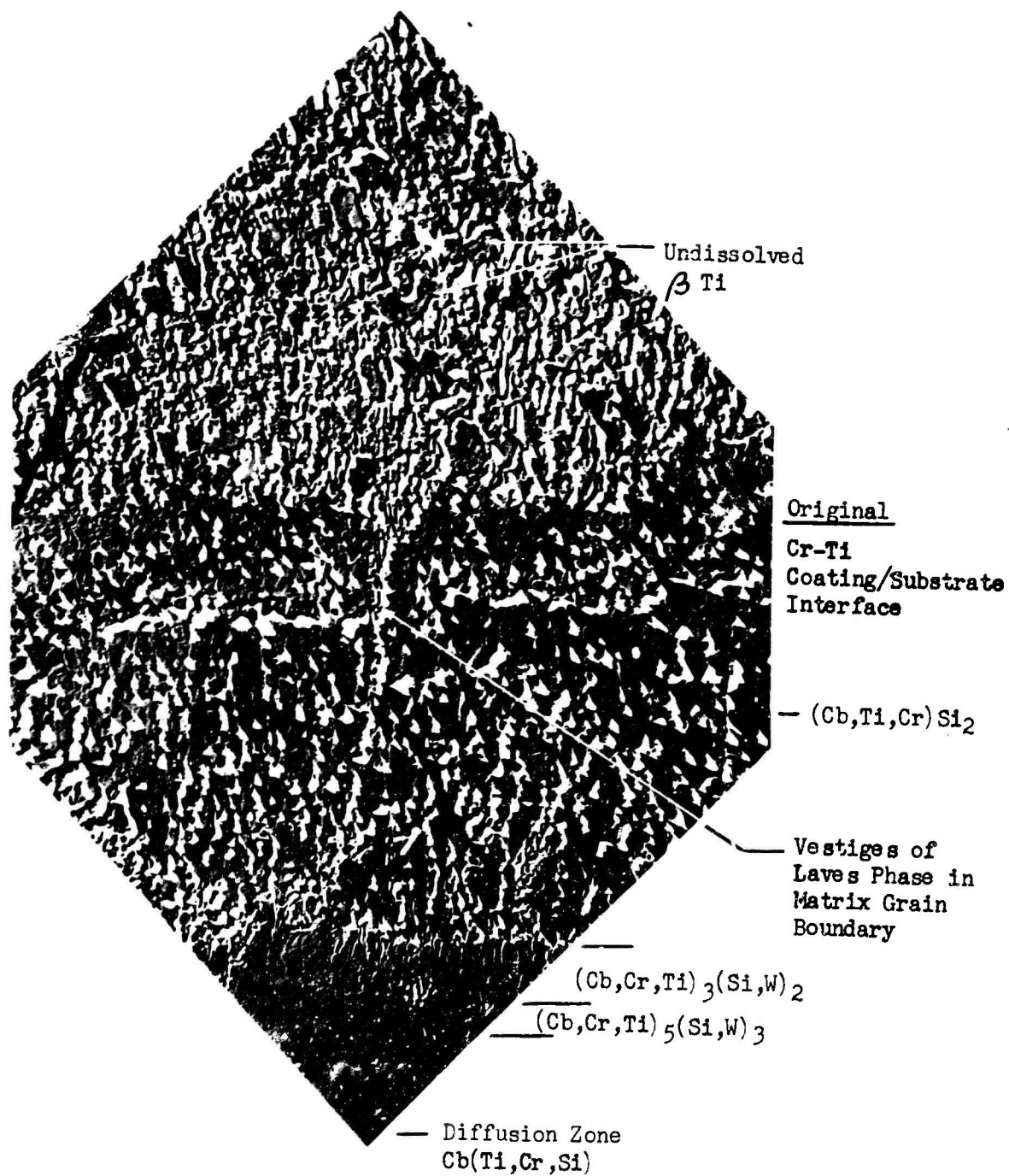
Mag: 6,000X

Figure 28 Electron Micrograph of Cr-Ti-Si Coated D-43 Alloy
(Specimen F)

55
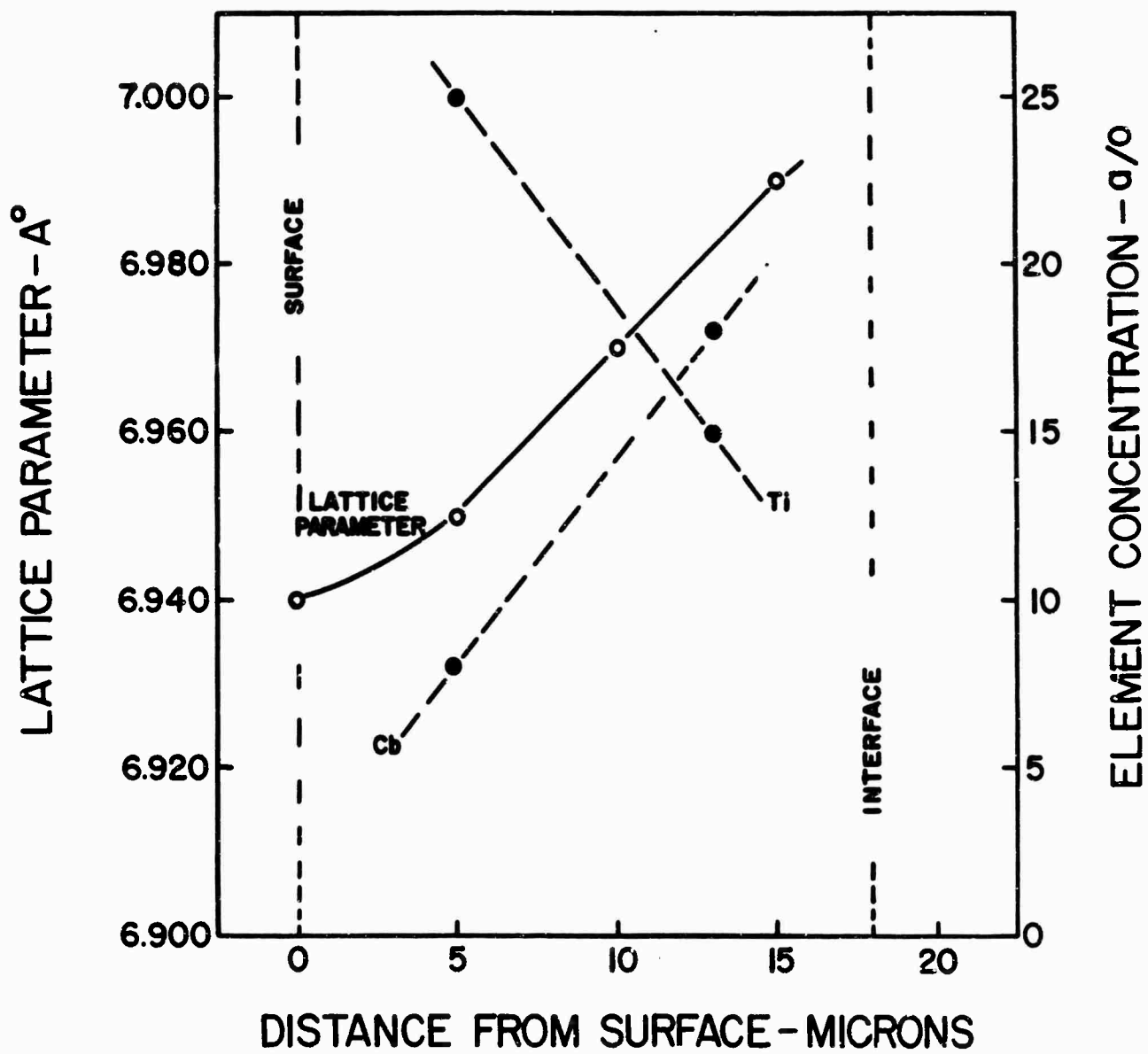
Figure 29 Lattice Parameter and Compositional Variation Across
(Cb,Ti)Cr$_2$ Phase of Cr-Ti Coating on D-43 Alloy

used was not sufficient for the precise detection of small differences in
d spacings. The bcc lines observed could have resulted from either the
β titanium phase or from the substrate beneath the Cr-Ti coating.
However, no additional lines were found in the diffraction pattern that
would indicate any other phase present. It is, therefore, concluded that
this phase is β titanium.

The diffractometer patterns from the Cr-Ti-Si coated coupon were quite
complex, and suggested that several phases were present across the Cr-Ti-Si
coating microstructure. Many of the diffraction lines which were very
pronounced in the outer regions of the disilicide were absent once the
surface had been removed to a depth beneath the original Cr-Ti/substrate
interface. The EMP results previously established that the composition of the
Cr-Ti-Si coating corresponded to a disilicide compound. However, the disili-
cides of chromium, titanium and columbium are not isomorphous ($CrSi_2$ and
$CbSi_2$ are hexagonal, whereas $TiSi_2$ is orthorhombic), thus, failure of the
X-ray data to fit one of these known patterns was not unexpected. The
pattern from the disilicide region which formed beneath the original Cr-Ti/
substrate interface agreed well with the reported X-ray pattern for $CbSi_2$.
This layer in the coating resulted from silicon penetration into the Cr-Ti-Cb
solid solution region beneath the original Laves phase, and was columbium
rich (15-18 a/o) as evidenced by the EMP. Many of the lines in the outer
disilicide region undoubtedly resulted from the inclusions or precipitates
which can be observed in this region of the microstructure. No attempt was
made to conduct an extensive X-ray analysis of the Cr-Ti-Si coating system
in this program, however, additional work in this area is being performed
by General Telephone and Electronics Laboratories under Contract AF 33(615)-
1685[8,9].

4.3 Oxidation Behavior of Cr-Ti-Si Coating

Cr-Ti-Si coated D-43 alloy coupons analogous to those analyzed in the
as-coated condition were exposed under various elevated temperature conditions
for further microstructural and compositional analysis. Eight exposure
conditions were investigated, in each case employing five replicate specimens.
Four exposures were performed in air at one atmosphere, and four at reduced
air pressures. The exposure parameters and the specimen notations are
listed in Table 10. Eight representative coupons were submitted to AMR
for electron microprobe analysis, and the remaining coupons were retained
for analysis by metallographic and electron microscopy techniques. In all
cases the freely exposed surface of the coupons was used for all analyses.
The results of these studies are discussed in the following subsections.

4.3.1 Electron Microprobe Analyses

The instrumentation and general methods utilized in probing the oxidized
specimens were identical with those employed previously in analyzing the
as-coated samples (Section 4.2.2). The analytical technique differed, however,
in that discrete point analyses were obtained rather than continuous beam

57

TABLE 10

Parameters for Oxidation Exposure of Cr-Ti-Si Coated
D-43 Specimens - Electron Microprobe Analysis

Specimen Notation	Exposure Conditions		
	Temperature °F	Time Hours	Pressure mm
U	1800	100	760
V	2500	4	760
W	2500	50	760
X	2700	4	760
M	2500	1	1
N	2500	4	1
O	2500	1	10^{-2}
P	2500	4	10^{-2}

58

traverses across the coating cross-sections. In the case of multi-phase and multi-layered alloys such as the Cr-Ti-Si coatings, data obtained by point analysis are more easily related to the alloy microstructures than are element intensity profiles obtained from a beam traverse. Figures 30 through 38 present the microprobe data and corresponding photomicrographs showing the precise location of each point analyses. In addition to analyzing the coating cross-sections, unmounted sections from the oxidized coupons were also employed to study the outer surface of the exposed coatings. A defocused beam ($\sim 200\mu$ diameter) was utilized in this case, such that the average compositions of the surface products were obtained. These data are tabulated as the surface chemistries in Figures 30 through 38. Figure 30 presents the probe data for the 100 hour - 1800°F - one atmosphere(U) exposure of the Cr-Ti-Si coating. The 1800°F exposure did not significantly alter either the coating microstructure or the compositional profile across the Cr-Ti-Si alloy. On the surface and at point(1) the composition is representative of an oxide-metal mixture, suggesting that only a thin superficial layer on the coating was converted completely to an oxide phase. The majority of the coating is still a disilicide, evidencing an increase in columbium and a decrease in chromium and titanium concentrations upon approaching the coating/substrate interface. Distinct boundaries are evident between the columbium and chromium (titanium) rich disilicides; and lower silicide bands are present adjacent to the substrate. A peak in the titanium concentration is observed at point(4), which represents the analysis of a discrete phase in the disilicide region. This titanium rich area resembles and undoubtedly corresponds to the β titanium phase which is observed as a dark secondary precipitate in the $(Cb,Ti)Cr_2$ Laves phase. It is also evident that the chromium and titanium are diffusing towards the surface of the coating to react with the oxygen.

Figures 31 and 32 show the microprobe data for the 4 and 50 hour 2500°F exposures of the Cr-Ti-Si coating at one atmosphere. It is obvious from these data that at 2500°F the chromium in the Cr-Ti-Si coating migrates very rapidly to the coating surface, while titanium and columbium diffuse towards the surface at somewhat slower rates. After 4 hours at 2500°F the surface oxides are basically Cr_2O_3 and TiO_2 (light phase), with a subsurface silicate having formed adjacent to the disilicide phase. After 50 hours at 2500°F (one atmosphere) the majority of the chromium had evaporated from the coating, possibly as a result of both pure chromium and chromium oxide vaporization. The absence of Cr_2O_3 on the scale surface suggests the vaporization of the oxide. The oxides remaining on the coating surface after 50 hours are essentially SiO_2 and TiO_2 (light phase), with a subsurface mixture of silica and possibly the complex oxide $TiO_2 \cdot Cb_2O_5$. Beneath the oxide scale is the remaining disilicide coating, which has been enriched with upwards of 15 w/o columbium. Lower silicide bands adjacent to the substrate are evidenced to have grown considerably in width. The substrate region beneath the silicide coating contains only silicon in solid solution, with all of the chromium and titanium having diffused from the original substrate diffusion zone into the outer regions of the coating. The latter three observations characterize the wearout

59

Coating	Cb	Ti	Si	Cr	Zr	W	Prototype Phases[1]
Surface	3	6	30	15	-	0.4	Metal·Oxides
1	4	8	28	16	-	0.5	Metal·Oxides
2	6	7	66	20	-	0.5	
3	6	7	64	22	-	1	$(Cr,Ti,Cb...)Si_2$
4	7	11	65	16	-	1	
5	10	6	66	16	-	2	
6	16	6	67	6	0.1	4	
7	17	5	68	5	0.1	4	$(Cb,Cr,Ti...)Si_2$
8	17	5	67	5	0.1	4	
9	55	6	42	6	0.3	5	$(Cb,Cr,Ti...)_3Si_2$
10	54	5	27	5	0.3	5	$(Cb,Cr,Ti...)_5Si_3$
Substrate							
1.8μ[2]	84	5	0.3	5	0.4	5.0	
3.5μ	84	5	0.2	5	0.5	5.4	
7.0μ	87	2	0.1	4	0.8	6.0	
10.5μ	92	-	0.05	0.5	0.8	6.2	
14.4μ	92	-	-	0.3	0.8	6.4	
21.2μ	93	-	-	0.1	0.8	6.5	
28.2μ	93	-	-	-	0.8	6.5	

Composition - a/o

(1) Based on element concentration only - principal phase(s)

(2) Distance perpendicular from interface

Sample U   540X

Figure 30

Cr-Ti-Si Coated D-43 Alloy
Exposed 100 Hours - 1800°F
One Atmosphere

60

Coating	Composition – a/o						Prototype Phases[1]
	Cb	Ti	Si	Cr	Zr	W	
Surface							
1	3	5	2	28	–	0.2	Cr₂O₃
2	7	18	1	10	–	0.5	TiO₂+Cr₂O₃
3	0.1	1	16	25	–	–	Cr₂O₃+SiO₂
4	6	12	66	16	–	0.5	(Cr,Ti,Cb...)Si₂
5	2	9	30	2	–	0.5	SiO₂+TiO₂
6	6	13	64	17	–	1	(Cr,Ti,Cb...)Si₂
7	4	12	66	17	–	1	
8	10	9	65	15	0.05	1	
9	12	5	66	15	0.05	2	
10	17	4	65	11	0.1	3	
11	22	3	65	7	0.1	4	(Cb,Cr,Ti...)Si₂
12	24	3	64	5	0.2	5	
13	47	3	39	4	0.3	6	(Cb,Cr,Ti...)₃Si₂
	53	2	38	2	0.3	6	(Cb,Cr,Ti...)₅Si₃
Substrate							
1.8µ (2)	86	0.5	4	2	0.5	6.4	
3.5µ	89	0.1	3	1	0.7	6.4	
7.9µ	92	–	0.5	0.5	0.7	6.4	
10.5µ	92	–	0.5	0.2	0.7	6.5	
14.1µ	93	–	–	0.1	0.8	6.5	
17.6µ	93	–	–	–	0.8	6.5	

(1) Based on element concentration only – principal phase(s)

(2) Distance perpendicular from interface

Sample V   540X

Figure 31

Cr-Ti-Si Coated D-43 Alloy
Exposed 4 Hours – 2500°F –
One Atmosphere

61
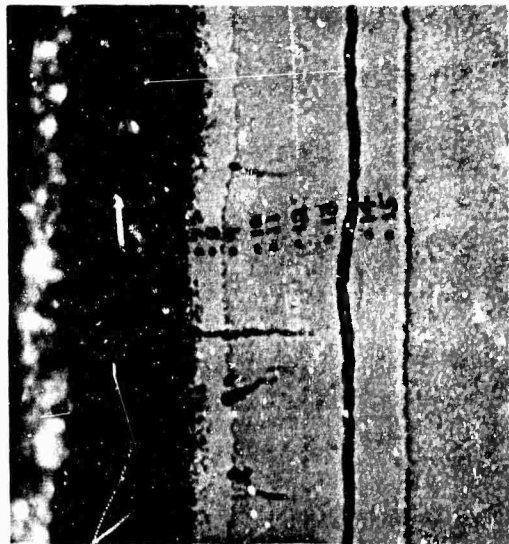
Sample W   54OX

Figure 32

Cr-Ti-Si Coated D-43 Alloy
Exposed 50 Hours – 2500°F
One Atmosphere

Coating	Composition – a/o						Prototype Phases(1)
	Cb	Ti	Si	Cr	Zr	W	
Surface	2	6	30	2	-	-	$SiO_2 + TiO_2$
1	4	28	0.2	2	0.1	0.1	TiO_2
2	0.1	3	18	3	-	-	SiO_2
3	10	10	20	5	-	1	$TiO_2 \cdot Cb_2O_5$ + SiO_2
4	12	10	5	2	-	1	
5	14	16	15	5	-	2	
6	15	10	67	6	0.1	2	$(Cb,Cr,Ti...)Si_2$
7	18	7	65	6	-	3	
8	22	4	65	5	0.1	4	
9	21	3	66	5	0.3	4	
10	22	2	66	4	0.3	5	
11	24	2	66	4	0.4	5	
12	50	1	41	2	0.5	6	$(Cb,Cr,Ti...)_5Si_3$
13	52	0.3	40	1	0.6	6	
14	53	-	39	0.6	0.7	6	$(Cb,Cr,Ti...)_3Si_2$
15	56	-	38	0.2	0.7	6	
Substrate							
1.8μ (2)	88	-	4	0.1	0.7	6.8	
3.5μ	90	-	3	-	0.7	6.5	
7.9μ	91	-	1	-	0.8	6.5	
10.5μ	93	-	-	-	0.8	6.5	

(1) Based on element concentrations only – principal phase(s)

(2) Distance perpendicular from interface

62

failure mechanism of the Cr-Ti-Si coating. The columbium disilicide and lower silicide phases are considerably less oxidation resistant than the originally formed chromium and titanium rich disilicide; and the depletion of chromium and titanium from the substrate renders the system more susceptible to localized failure at coating cracks or fissures.

Figure 33 presents the EMP data for the 4 hour - 2700°F exposure of the Cr-Ti-Si coating in one atmosphere air. In contrast to the 4 hour exposure at 2500°F, where the surface oxide was Cr_2O_3, the surface oxides remaining after 4 hours at 2700°F were basically TiO_2 (light phase) and SiO_2. The oxides adjacent to the disilicide, on the other hand, were Cr_2O_3 and silica. At 2700°F the vaporization rate of chromium (oxide) from the coating apparently exceeded the rate at which chromium could diffuse to the surface, leaving basically the oxides of silicon and titanium. The disilicide immediately adjacent to the oxide scale is a chromium rich disilicide phase. Note the absence of titanium and the low concentration of chromium in the substrate beneath the silicide, and also the peak in the tungsten content near the substrate-coating interface. The two coating constituents diffuse outward very rapidly at 2700°F thereby depleting the substrate, however, the reason for the peak in the tungsten concentration is not clear.

Figure 34 is a graph showing EMP data obtained by Solar(4) on a diffusion annealed (argon - 24 hours - 2500°F) Cr-Ti-Si coated B-66 alloy. These data describe the intermetallic compositions, evidencing the lower silicide phases and a phase containing a constant metal to silicon ratio of 6:5. It is doubtful that the coatings on these two substrates would differ appreciably after the similar 2500°F exposures, since they did not in fact differ significantly in the as formed condition (Section 4.1.2). It appears that some discrepancy may exist between the two independent EMP analyses.

Figures 35 and 36 present the EMP data for specimens exposed 1 and 4 hours at 2500°F in air at 1 mm pressure. Weight change analyses of the coupons indicated an initial weight increase of 2.8 mg (1 hour), followed by a weight loss, resulting in a net weight gain of 1.7 mg after 4 hours. The coupons were 1/2" x 1/2" sheet specimens, and one side of the coupon was in intimate contact with the alumina support material. After both 1 and 4 hour exposures the principal oxide on the coating was Cr_2O_3, intermixed with the oxides of titanium and silicon. The relative presence of chromium at the surface increased with time, supporting the observed weight loss which resulted from the outward migration and subsequent vaporization of chromium. The unoxidized particle in the oxide layer (point 5) is a disilicide phase, rich in columbium and lean chromium in comparison with the adjacent disilicide phase, indicating a depletion and selective oxidation of the chromium from the phase. Comparing the 4 hour/2500°F exposures at one atmosphere and at 1 mm pressure, the microstructures and compositions are not markedly different. The only significant differences are (1) the thicker oxide formed at one atmosphere and (2) the higher titanium content

63

Coating	Cb	Ti	Si	Cr	Zr	W	Prototype Phases(1)
Surface	3	11	11	3	-	0.2	——— TiO_2, SiO_2
1	5	27	1	2	0.1	0.6	——— TiO_2
2	-	3	14	5	-	-	——— SiO_2
3	2	2	19	28	-	-	——— $Cr_2O_3 + SiO_2$
4	1	5	6	36	-	0.2	——— Cr_2O_3
5	6	10	65	19	-	0.5	$(Cr,Ti,Cb...)Si_2$
6	5	9	67	20	-	0.5	
7	8	11	66	14	-	1	
8	12	8	64	14	0.1	2	
9	17	5	63	11	0.1	3	$(Cb,Cr,Ti...)Si_2$
10	15	4	64	14	0.1	3	
11	17	3	65	12	0.1	4	
12	18	3	65	8	0.2	4	
13	42	3	40	7	0.3	6	$(Cb,Cr,Ti...)_3Si_2$
14	52	1	39	3	0.5	5	$(Cb,Cr,Ti...)_5Si_3$
15	53	0.5	39	2	0.6	5	
Substrate							
0.9μ (2)	89	-	2	0.5	0.6	7.5	
2.6μ	92	-	0.4	0.3	0.6	6.5	
4.4μ	92	-	0.1	0.3	0.6	5.5	
7.9μ	93	-	0.05	0.2	0.8	6.5	
10.6μ	93	-	0.05	0.1	0.8	6.5	
17.6μ	93	-	-	0.1	0.8	6.5	
24.8μ	93	-	-	-	0.8	6.5	

Composition – a/o

(1) Based on element concentration only – principal phase(s)

(2) Distance perpendicular from interface

540X

Sample X

Figure 33

Cr-Ti-Si Coated D-43 Alloy
Exposed 4 Hours – 2700°F –
One Atmosphere
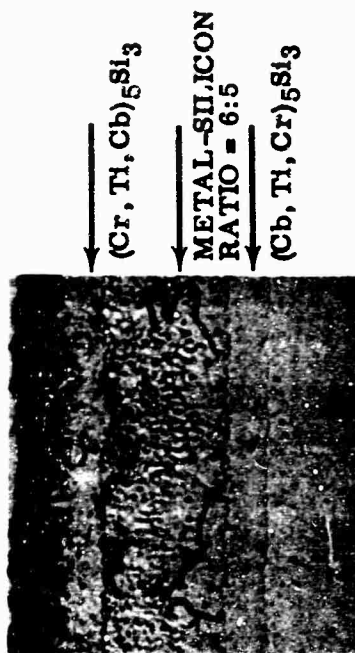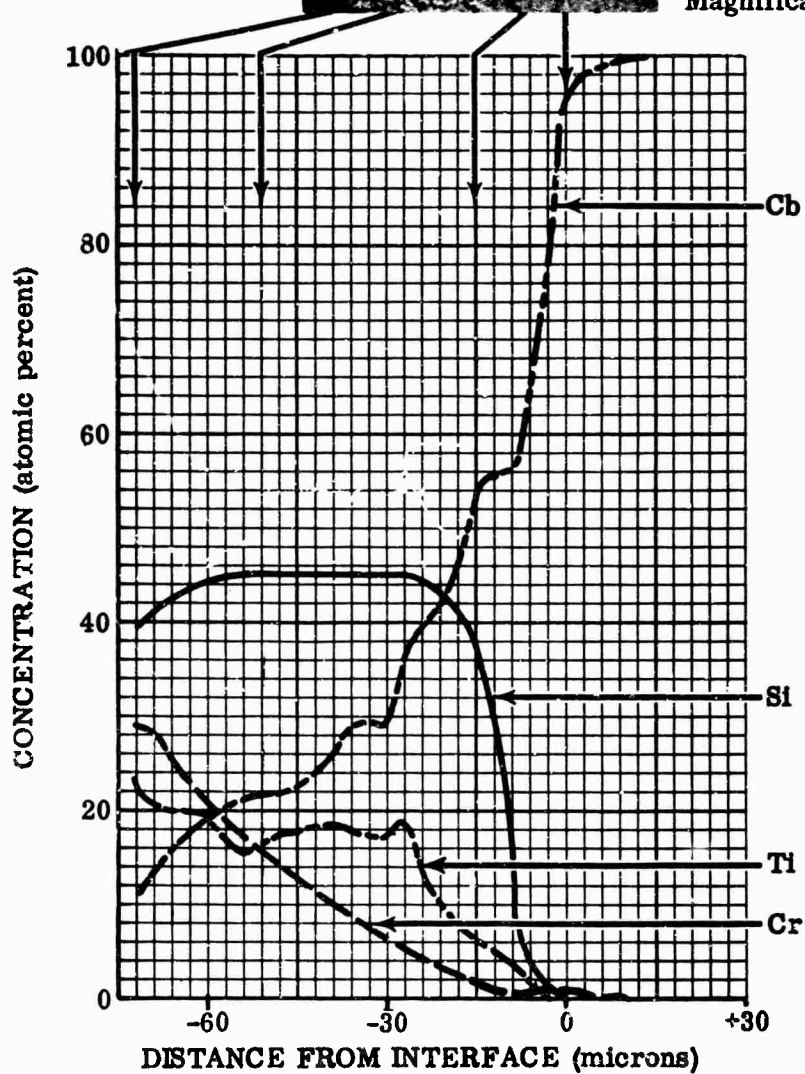
Figure 34 Concentration – Penetration Profile of the Cr-Ti-Si Coating on B-66 Alloy; Diffusion – Annealed 24 Hours at 2500° F(4)

65
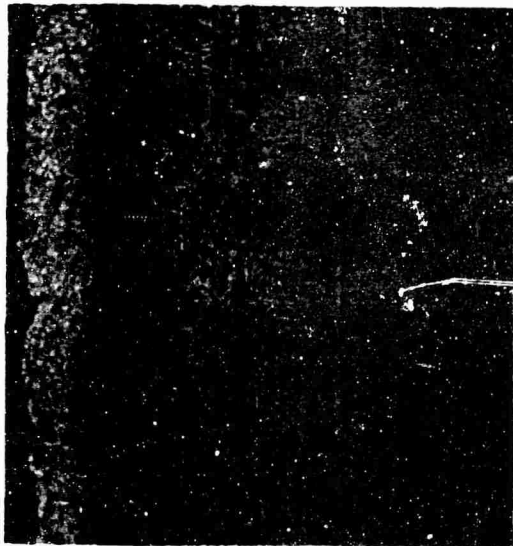
Sample M   540X

Figure 35

Cr-Ti-Si Coated D-43 Alloy
Exposed 1 Hour – 2500°F –
1 mm

Coating	Cb	Ti	Si	Cr	Zr	W	Prototype Phases(1)
Surface	3	8	4	20	–	–	Cr₂O₃+TiO₂
1	1	2	14	25	–	–	Cr₂O₃+SiO₂
2	1	10	27	17	–	0.5	Metal Oxides
3	6	13	65	15	–	0.5	
4	4	7	65	23	–	0.8	
5	6	11	64	20	–	0.8	(Cr,Ti,Cb...)Si₂
6	9	11	65	15	–	1	
7	9	7	65	19	0.1	1	
8	17	5	56	7	–	4	
9	20	4	66	5	–	4	(Cb,Cr,Ti...)Si₂
10	22	2	68	3	0.1	4	(Cb,Cr,Ti...)₃Si₂ + (Cb,Cr,Ti...)₅Si₃
11	51	1	42	2	0.3	5	(Cb,Cr,Ti...)₅Si₃
Substrate							
1.8μ (2)	91	0.3	0.5	0.3	0.7	6.6	
3.5μ	92	–	–	0.3	0.8	6.5	
7.0μ	92	–	–	0.3	0.8	6.5	
10.5μ	92	–	–	0.3	0.8	6.5	
14.1μ	93	–	–	0.1	0.8	6.5	
17.6μ	93	–	–	–	0.8	6.5	

Composition - a/o

(1) Based on element concentration only – principal phase(s)

(2) Distance perpendicular from interface

66

Coating	Composition - a/o						Prototype Phases[1]
	Cb	Ti	Si	Cr	Zr	W	
Surface	3	7	1	30	-	-	Cr$_2$O$_3$+TiO$_2$
1	1	2	10	25	-	-	Cr$_2$O$_3$+SiO$_2$
2	1	5	2	34	-	-	Cr$_2$O$_3$
3	3	6	6	6	-	0.8	Mixed Oxides (Porosity)
4	2	8	20	9	-	0.6	SiO$_2$
5	11	12	65	11	-	1	⎫
6	5	10	66	19	-	0.6	⎬ (Cr,Ti,Cb...)Si$_2$
7	8	11	65	16	-	1	⎭
8	10	7	67	14	0.1	2	
9	12	9	66	10	0.1	2	
10	17	4	66	7	0.1	5	⎫
11	19	3	68	4	0.1	5	⎬ (Cb,Ti,Cr...)Si$_2$
12	23	3	65	3	0.2	5	⎭
13	43	3	42	6	0.2	6	⎫ (Cb,Cr,Ti...)$_5$Si$_2$
14	50	2	40	2	0.4	6	⎭
15	52	1	39	2	0.4	6	(Cb,Cr,Ti...)$_5$Si$_3$
Substrate							
1.8μ[2]	91	0.6	0.6	1.6	0.7	6.0	
3.5μ	92	0.2	0.2	1.0	0.8	6.0	
5.3μ	92	-	0.1	0.5	0.8	6.2	
7.9μ	92	-	0.05	0.1	0.8	6.5	
8.8μ	93	-	-	0.05	0.8	6.5	
10.5μ	93	-	-	-	0.8	6.5	

(1) Based on element concentration only - principal phase(s)

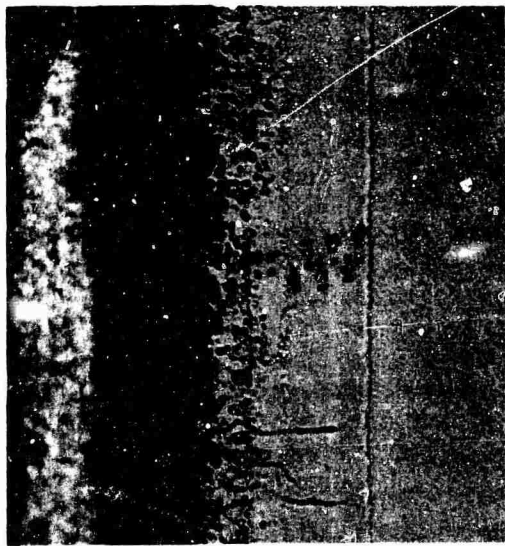(2) Distance perpendicular from interface

Sample N   540X

Figure 36

Cr-Ti-Si Coated D-43 Alloy
Exposed 4 Hours - 2500°F -
1 mm

67

8391

of the oxides formed at one atmosphere.

Figures 37 and 38 present the EMP data for the 1 and 4 hour - 2500°F exposures of the Cr-Ti-Si coating at 10^{-2} mm. After 1 hour exposure the surface evidenced a mixture of oxides containing all of the coating elements and a relatively high concentration of columbium (10 w/o). Exposure for 4 hours resulted in the vaporization of virtually all of the chromium from the surface oxide, leaving an oxide scale which corresponds to TiO_2 and possibly the complex oxide $TiO_2 \cdot CbO_5$. The rate of diffusion of chromium through the scale to the free surface was significantly lower than the rate of chromium vaporization. The very low concentration of silicon throughout the oxide scale (4 hour exposure) indicates that significant SiO vaporization also occurred at 10^{-2} mm. It has been shown by post oxidation testing that reduced pressure exposure of the Cr-Ti-Si coating causes considerable degradation of the coating protective properties. The loss of properties is apparently associated with the relatively high concentration of columbium in the remaining disilicide, and failure of the disilicide to form an impervious protective oxide when subsequently exposed at one atmosphere. The titanium and columbium oxides are not protective, and apparently these surface oxides also impede the formation of a protective scale on the remaining disilicide.

A summary of these EMP results on the exposed Cr-Ti-Si coatings will be presented in Section 4.4, along with the overall summary of the Cr-Ti-Si system analysis.

4.3.2 Electron Microscopy

Electron microscopy was again employed to further study the oxidation exposed Cr-Ti-Si coatings. The procedures used in preparing the surface replicas were outlined in Section 4.2.2. Figures 39 through 42 show four composite electron micrographs representing the highly magnified microstructures of four of the exposed specimens. The approximate location of the EMP point analyses and the corresponding prototype phases are noted on each electron micrograph. The four specimens represented are V, X, M and O, and the numbers of the point analyses correspond to the chemistries tabulated for these loca-tions in Figures 31, 33, 35 and 37, respectively.

In general, the electron micrographs added only moderately to the observations already made on the light micrographs. It is clearly shown from the highly magnified replicas that very sharp boundaries delineate the several disilicide phases across the coating. In some cases these phases differ only slightly in the relative concentrations of chromium, titanium and columbium. However, it is also evident that considerable solubility for the various constituents also exists within each phase boundary. Most of the diffusion bands are also evidenced as two phase regions, indicating that the precipitation of secondary phases occurred at the cooling rate represented by air cooling of the coupons. Solar has shown that by water quenching the Cr-Ti-Si coating from 2500°F, certain

68

Coating	Cb	Ti	Si	Cr	Zr	W	Prototype Phases(1)
			Composition ~ %				
Surface	10	15	18	9	-	0.6	Mixed Oxides
1	7	15	19	19	-	0.5	
2	7	15	20	18	-	0.5	
3	6	10	64	19	-	1	$(Cr,Ti,Cb...)Si_2$
4	5	8	65	21	-	1	
5	7	12	66	14	-	1	
6	10	7	65	16	0.07	2	
7	12	7	64	15	0.07	2	
8	19	3	66	7	0.1	5	$(Cb,Cr,Ti...)Si_2$
9	22	3	65	5	0.2	5	
10	25	3	64	4	0.2	5	
11	50	3	38	3	0.3	6	$(Cb,Cr,Ti...)_3Si_2$ + $(Cb,Cr,Ti...)Si$
Substrate							
1.8μ (2)	86	3	0.5	4	0.6	6.0	
3.5μ	89	1	0.2	3	0.7	6.0	
5.3μ	90	1	0.1	2	0.8	6.1	
7.0μ	92	-	-	0.4	0.6	6.5	
10.5μ	93	-	-	0.1	0.8	6.5	
14.1μ	93	-	-	0.1	0.9	6.5	
21.2μ	93	-	-	-	0.8	6.5	

(1) Based on element concentration only - principal phase(s)

(2) Distance perpendicular from interface

Sample O   540X

Figure 37

Cr-Ti-Si Coated D-43 Alloy
Exposed 1 Hour - 2500°F -
10^{-2} mm
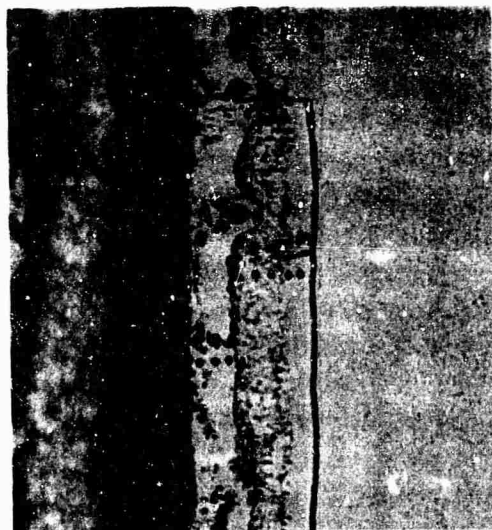
Sample P 540X

Figure 38

Cr-Ti-Si Coated D-43 Alloy
Exposed 4 Hours – 2500°F –
10^{-2} mm

Coating	Composition – a/o						Prototype Phase(1)
	Cb	Ti	Si	Cr	Zr	W	
Surface	12	20	1	1	–	1.0	TiO$_2$·Cb$_2$O$_5$
1	1	18	2	2	–	0.5	TiO$_2$
2	12	19	0.2	1	0.1	0.5	TiO$_2$·Cb$_2$O$_5$
3	8	19	6	2	0.1	0.8	
4	8	13	63	15	0.1	1	(Cr,Cb,Ti...)Si$_2$
5	13	4	66	16	0.1	2	
6	8	8	65	19	–	1	
7	8	13	63	15	0.1	1	
8	13	4	66	16	0.1	2	
9	16	3	66	11	0.1	4	(Cb,Cr,Ti...)Si$_2$
10	22	2	64	8	0.1	4	
11	23	2	65	5	0.2	5	(Cb,Cr,Ti...)$_5$Si$_3$
12	46	2	41	5	0.3	5	
13	51	2	39	3	0.4	5	(Cb,Cr,Ti...)$_5$Si$_3$
14	52	1	39	2	0.4	5	
Substrate							
1.8μ(2)	90	0.2	1.4	1.6	0.5	6.5	
3.5μ	91	0.2	0.3	1.4	0.5	6.5	
5.3μ	92	0.2	0.1	0.8	0.6	6.5	
7.0μ	92	–	0.05	0.6	0.8	6.5	
8.8μ	92	–	0.05	0.3	0.8	6.5	
10.5μ	92	–	–	0.2	0.8	6.5	
14.1μ	93	–	–	0.05	0.8	6.5	
17.6μ	93	–	–	–	0.8	6.5	

(1) Based on element concentration only – principal phase(s)
(2) Distance perpendicular from interface

70

-(6) ——— $(Cr,Ti,Cb...)Si_2$

-(7) ⎤

⎥ $(Cr,Cb,Ti...)Si_2$

-(8) ⎦

-(9) ⎤

-(10) — $(Cb,Cr,Ti...)Si_2$

-(11) ⎦

-(12) — $(Cb,Ti,Cr...)_3Si_2$

Figure 39 Cr-Ti-Si Coated D-43 Alloy - 4 Hours - 2500°F -
One Atmosphere(V)   Mag: 6,000X

71
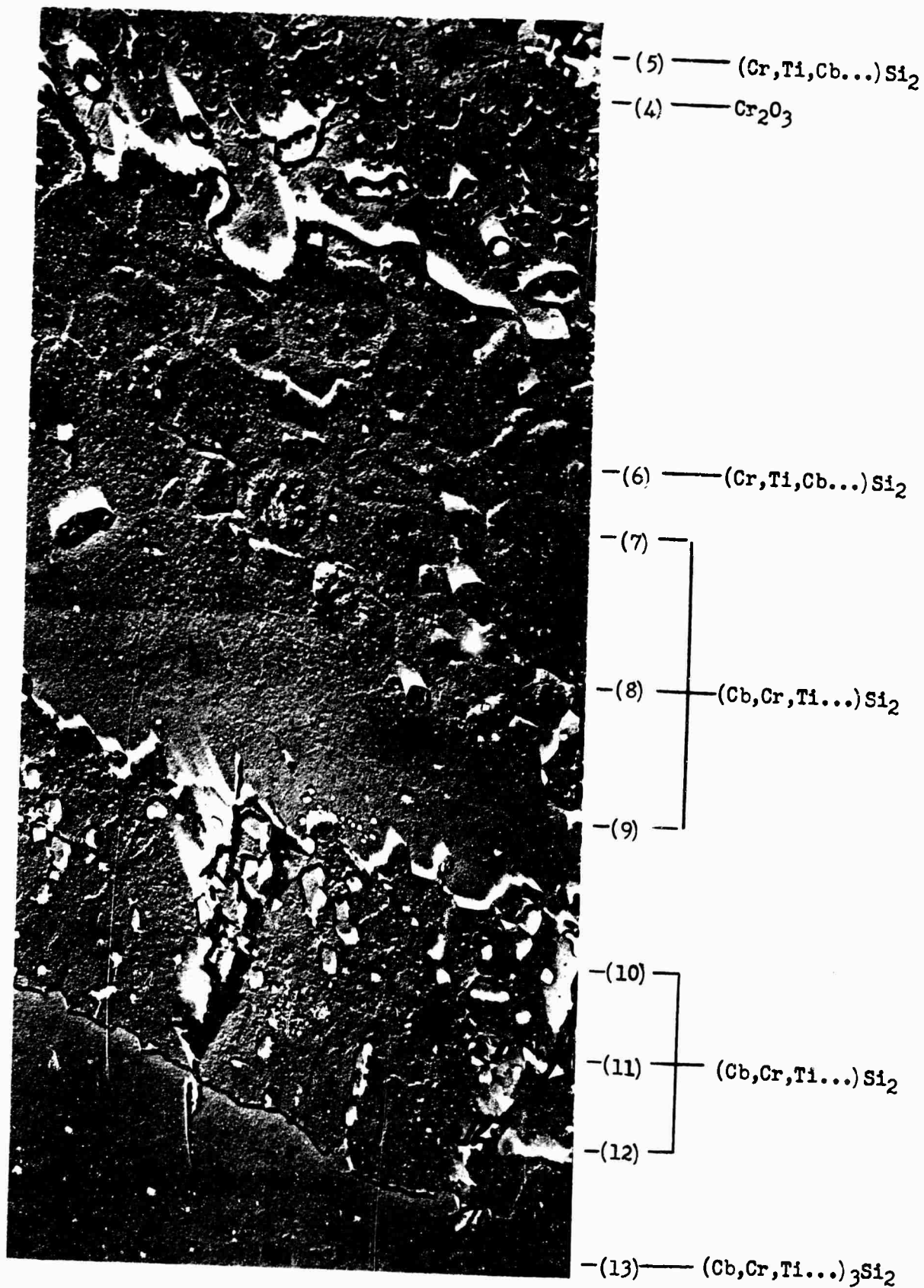
Figure 40 Cr-Ti-Si Coated D-43 Alloy - 4 Hours - 2700°F - One
Atmosphere (X)
Mag: 6,000X

-(6) —— $(Ti,Cr,Cb...)Si_2$

-(7) —— $(Cr,Cb,Ti...)Si_2$

-(8)

-(9) —— $(Cb,Cr,Ti...)Si_2$

-(10)

-(11)—— $(Cb,Cr,Ti...)_3Si_2$
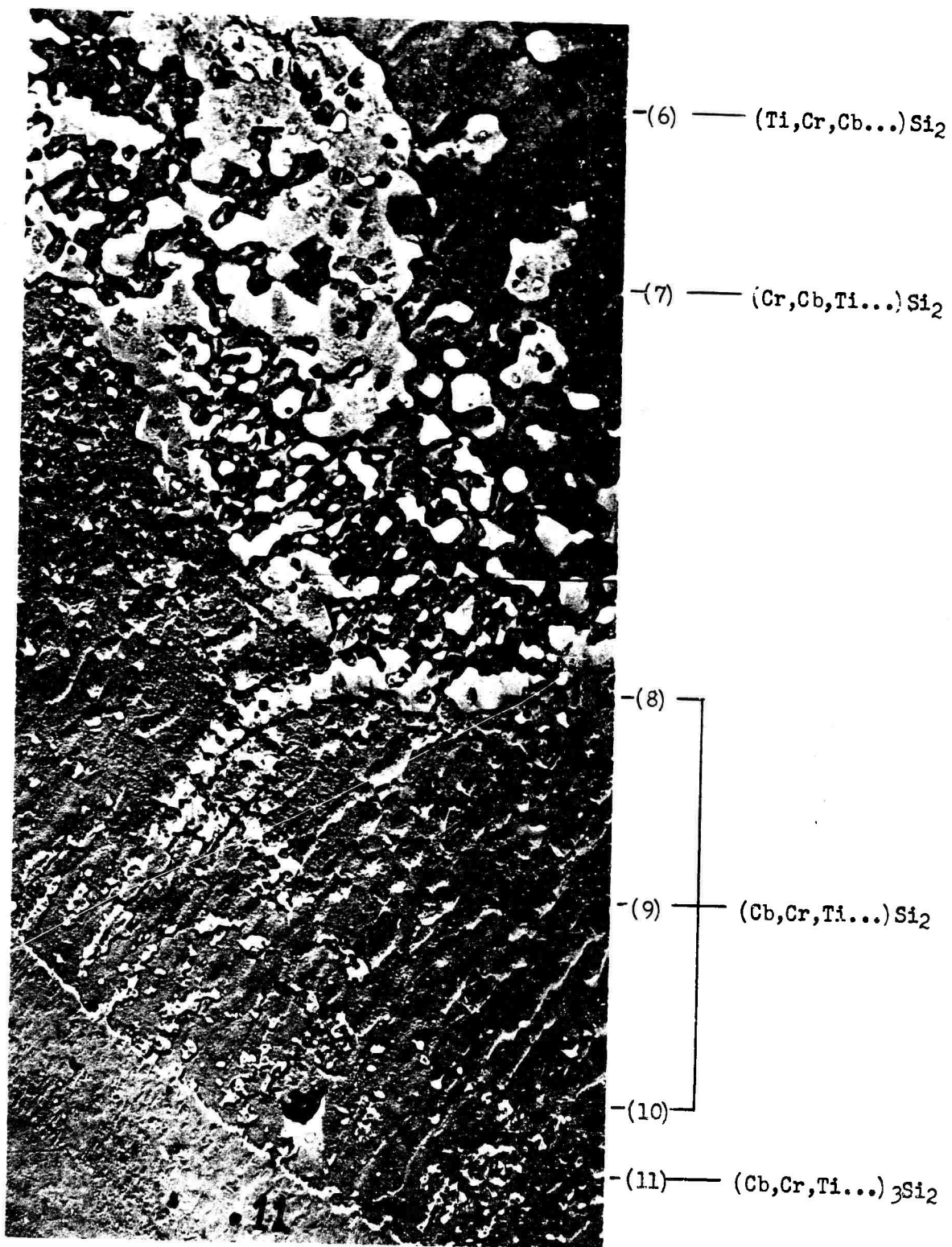
Figure 41   Cr-Ti-Si Coated D-43 Alloy - 1 Hour - 2500°F -
1 mm (M)   Mag: 6,000X
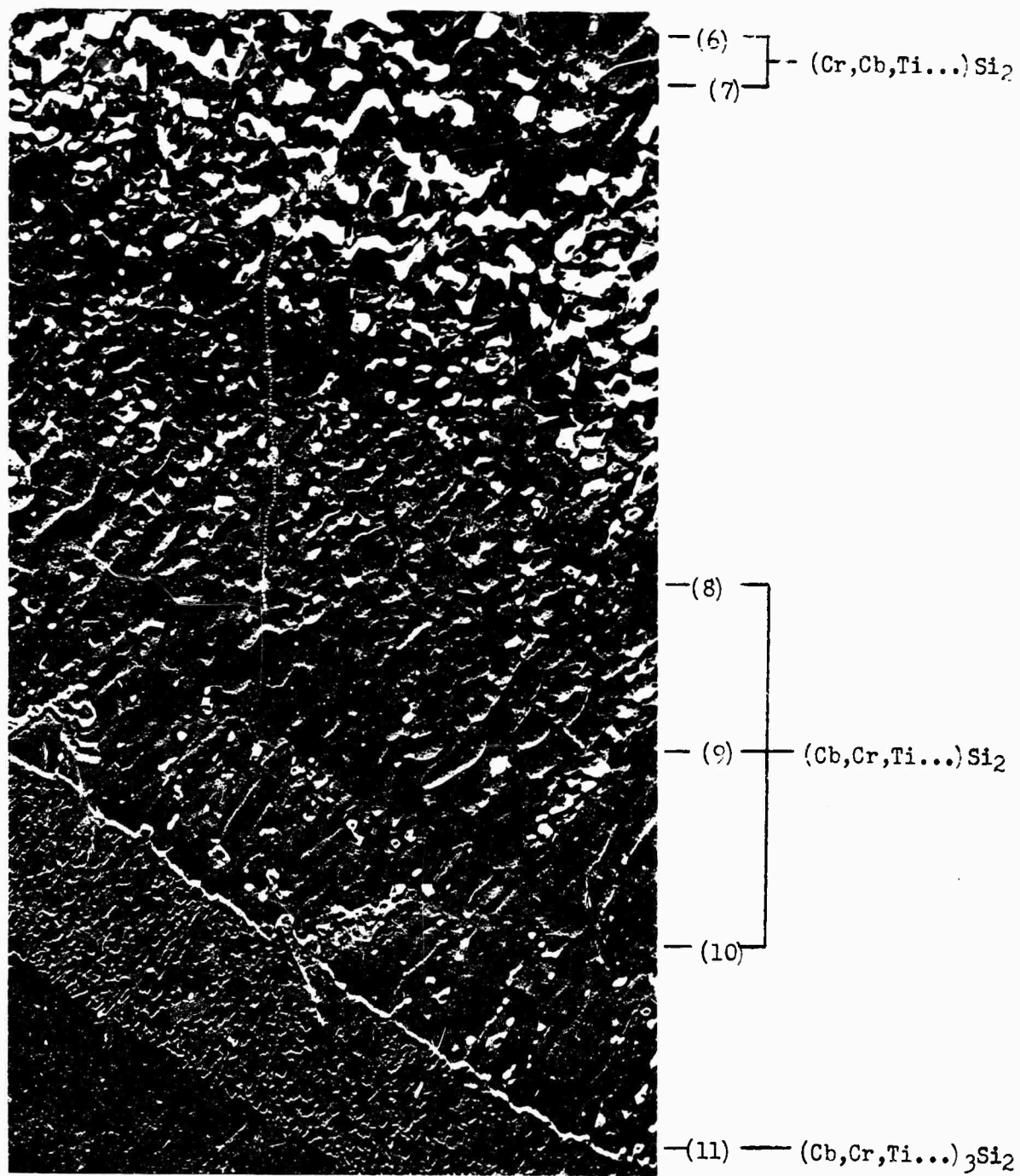
Figure 42 Cr-Ti-Si Coated D-43 Alloy - 1 Hour - 2500°F -
10⁻² mm (0)   Mag: 6,000X

74

intermetallic phases are retained in solid solution[4]. Precipitation of these phases was accomplished by Solar utilizing an aging treatment at 1750°F.

4.3.3 Oxidation Weight Change

A study was made of the weight change incurred by Cr-Ti-Si coated D-43 alloy during exposure in air (one atmosphere) at various temperatures from 1800 to 2800°F. The test specimens (area = 5.5 cm²) were suspended in a globar heated air furnace from the arm of a chainomatic balance. An aluminum oxide support fixture was in contact with the coated surface. The specimen weight change was monitored during the static oxidation exposure and continuous weight change curves were delineated. It was assumed that all weight change was attributed to oxidation or coating element vaporization, i.e., it was assumed the coating did not flake or spall in the absence of thermal cycling or handling. Replicate specimens were tested at all temperatures from 1800 to 2800°F, and these weight change data are plotted as a function of exposure time in Figures 43 through 46. Figure 47 is an additional log-log plot of the 1800, 2000 and 2300°F data.

At 1800°F the oxidation rate of the Cr-Ti-Si was parabolic, resulting in a weight gain of only 0.7 mg/cm² in 200 hours of exposure. At 2000 and 2300°F the initial rate of oxidation was parabolic; breakaway to a linear or faster rate then occurred after 5-10 hours; and after 50-100 hours the oxidation rate again reverted to essentially a parabolic character. The intermediate increase in the rate of oxidation was apparently a geometrically induced behavior, not characteristic of the coating system. Based on both visual (external) and metallographic evidence, the increased oxidation rate apparently resulted from preferential edge oxidation on the sheet coupons, owing to the opening of cracks and the exposure of unoxidized coating surface. Figure 48 shows a typical edge crack and the penetration of oxide scale on a specimen tested at 2300°F. Eventually sufficient cracking occurred to relieve the tensile stresses and the rate of oxidation decreased to essentially a parabolic rate. The loss of weight after 30-40 hours of exposure at 2300°F is attributed to either chromium vaporization from the coating or very light spalling at the coupon edges.

At 2500°F and above the Cr-Ti-Si coating exhibited an initial weight gain, followed by a continuous weight loss until a point of rapid oxidation or breakaway was encountered. The abrupt increase in the rate of oxidation was the result of localized coating failures in the specimen support area, and the attendant oxidation of the columbium substrate.

Two weight change mechanisms were competing in the early stages of the higher temperature oxidation exposures: 1) a weight increase attributed to oxidation of the coating, and 2) a weight loss associated with the vaporization of chromium and possibly silicon from the coating. The rate of loss increased with increasing temperature, as evidenced by the corresponding decrease in the time at which the weight change curves crossed zero on

75
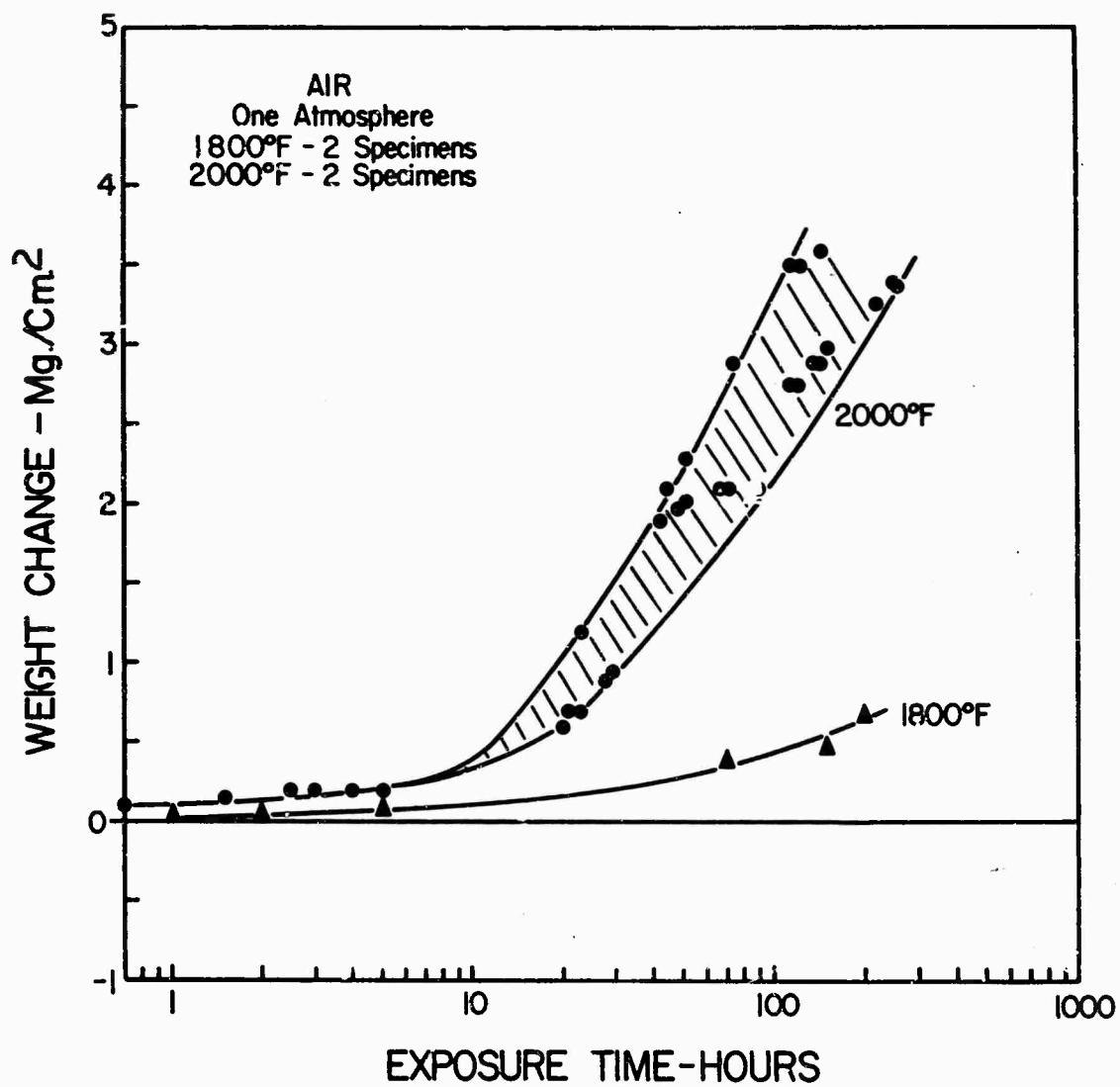
Figure 43 Weight Change as a Function of Time for Oxidation of Cr-Ti-Si Coated D-43 Alloy in Air at 1800 and 2000° F

76
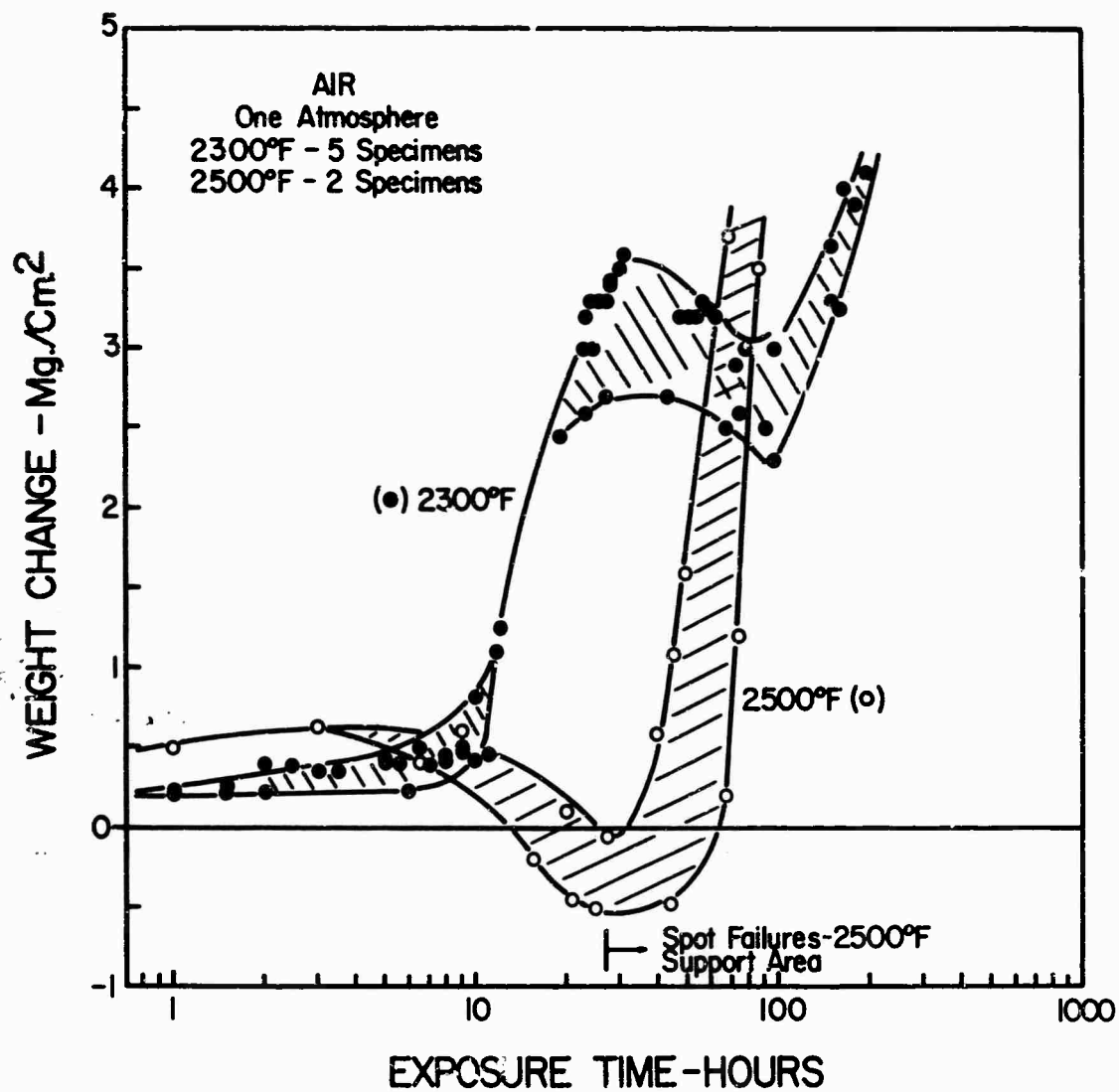
Figure 44 Weight Change as a Function of Time for Oxidation of Cr-Ti-Si Coated D-43 Alloy in Air at 2300 and 2500°F
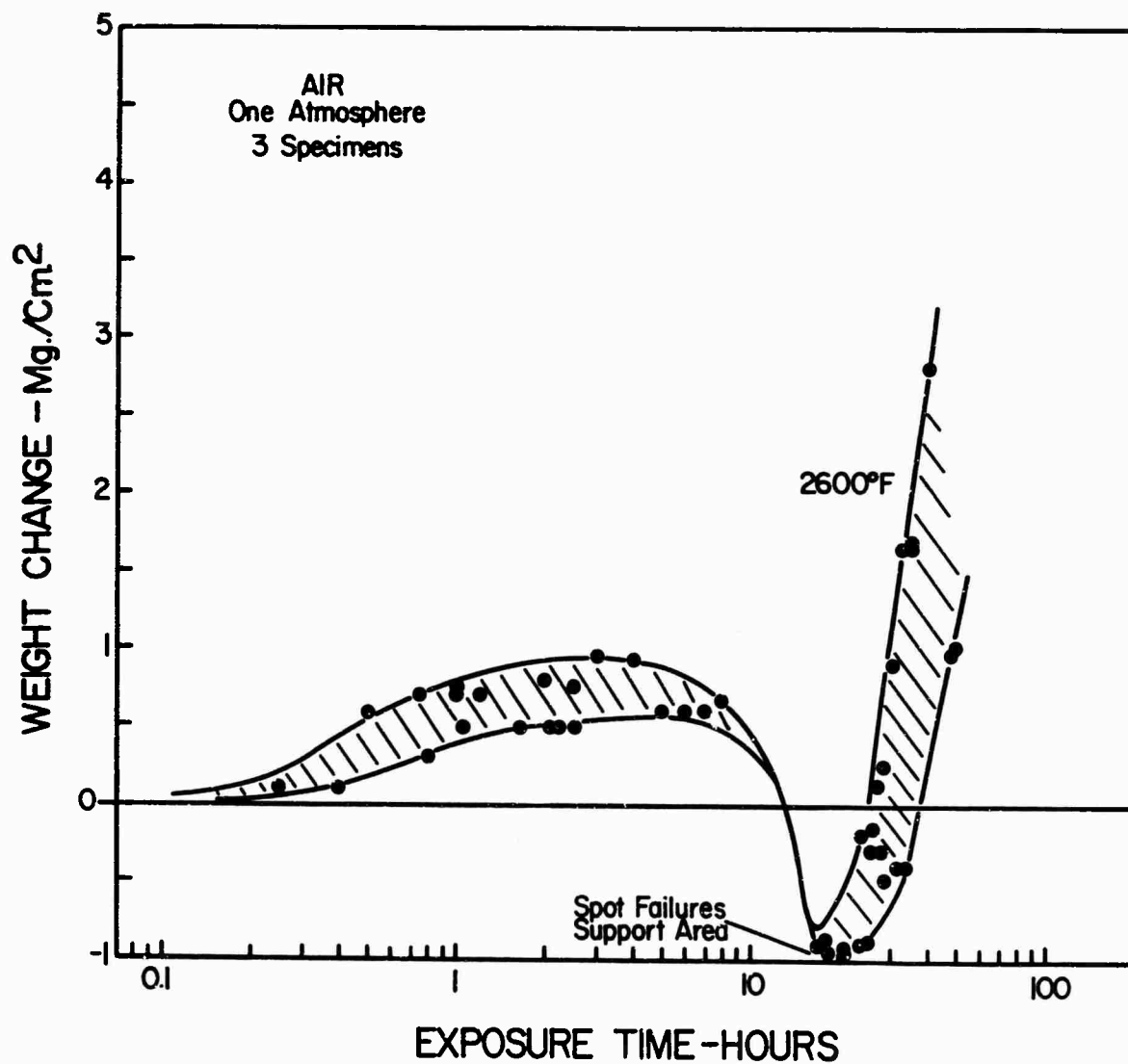
Figure 45   Weight Change as a Function of Time for Oxidation of Cr-Ti-Si Coated
D-43 Alloy in Air at 2600°F

78
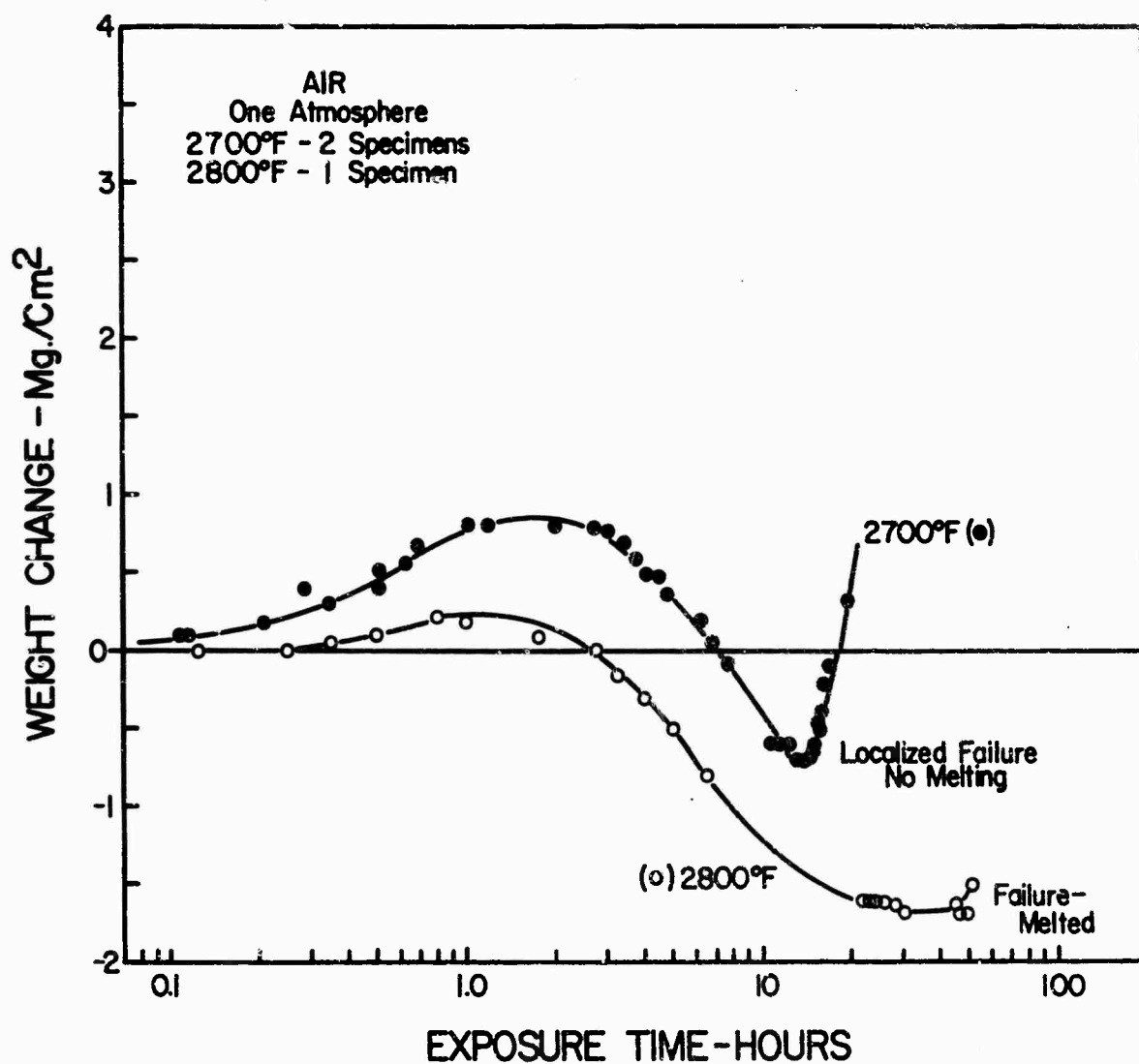
Figure 46   Weight Change as a Function of Time for Oxidation of Cr-Ti-Si Coated D-43 Alloy in Air at 2700 and 2800°F
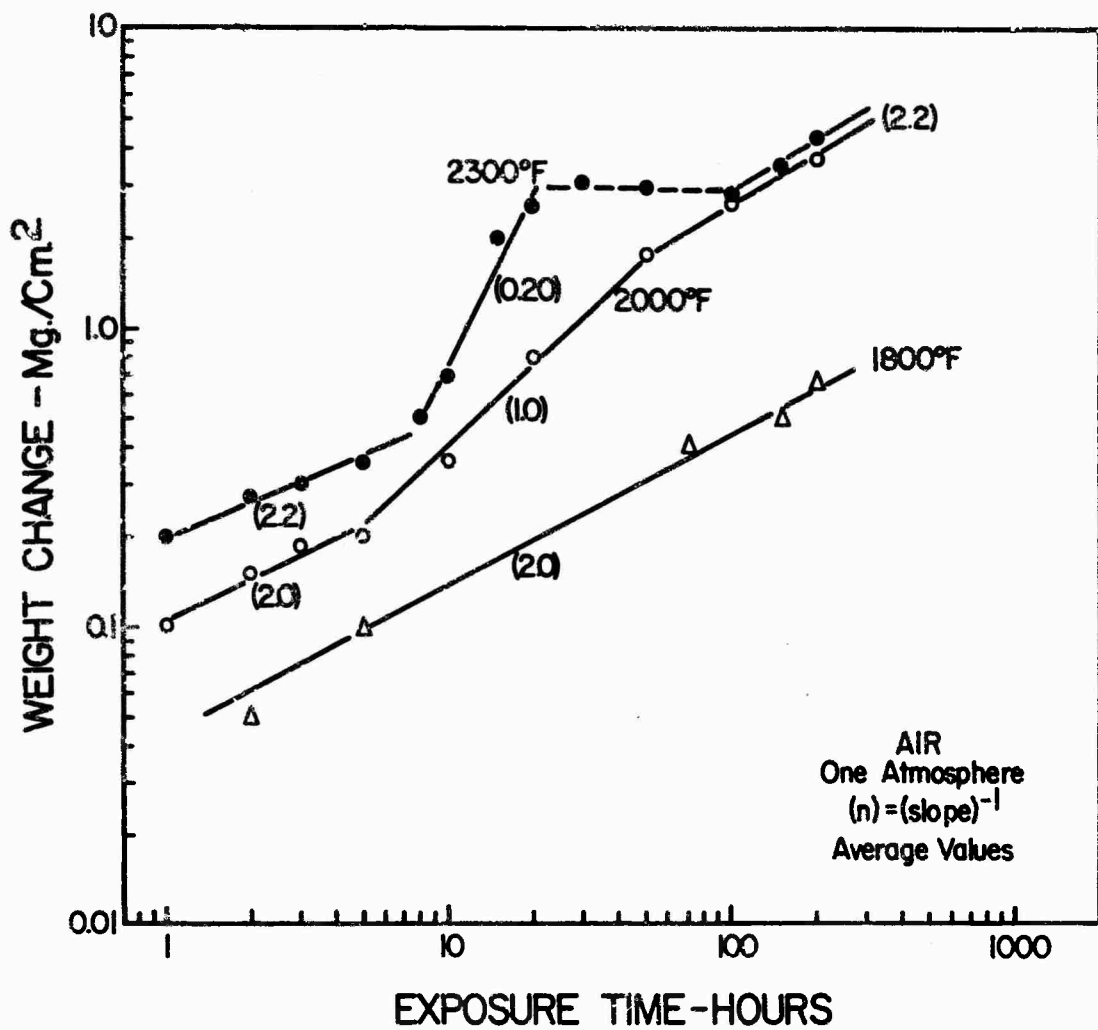
Figure 47 Log-Log Plot of Weight Gain as a Function of Time for Oxidation Testing of Cr-Ti-Si Coating in Air at 1800, 2000 and 2300°F

Edge Crack - Scale Formation
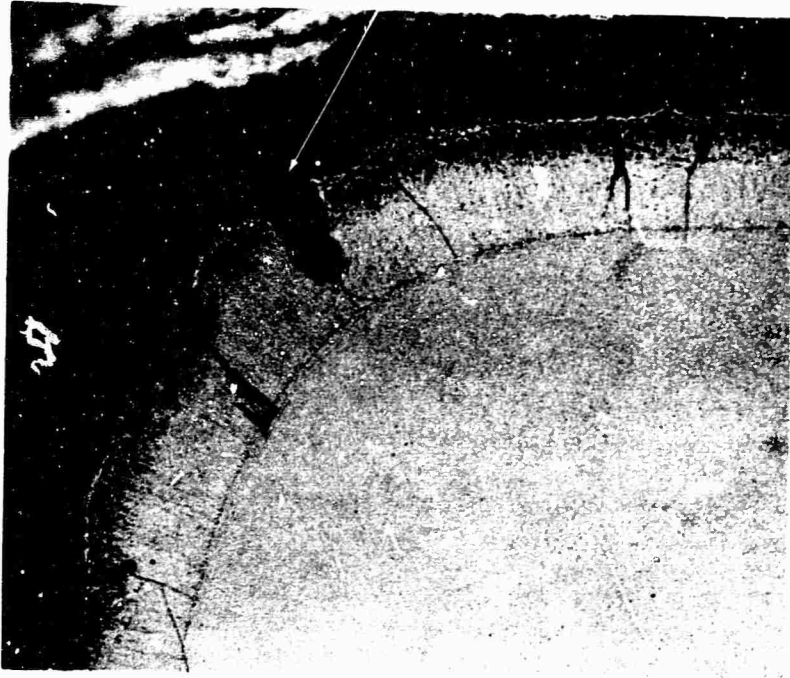
31 Hours   2300°F (Air)

Cr-Ti-Si Coated D-43

Figure 48 Photomicrograph Showing Edge Cracking and Oxidation of
          Cr-Ti-Si Coating on D-43 Alloy - 2300°F   250X

81

the ordinate. Less than 1 mg/cm^2 was lost at temperatures from 2500 to 2700°F, however, at 2800°F the coating weight loss exceeded 1.5 mg/cm^2. It is interesting to note that the time at which localized coating failures occurred was greater at 2800°F than at temperatures from 2500 to 2700°F. There is no obvious explanation for this behavior, and, this has not generally been the case in cyclic oxidation tests on the Cr-Ti-Si coating.

4.4 Summary of Cr-Ti-Si System Analysis

The Cr-Ti-Si coating is a diffusion alloy surface layer formed on columbium substrates by a two cycle vacuum pack process. The initial cycle involves the co-deposition of chromium and titanium, followed by a siliconizing cycle. A Laves phase overlay of the form $(Cb,Ti)Cr_2$ is formed on the substrate during the Cr-Ti coating cycle; and with some columbium alloys (D-43, D-31 and D-41) this phase evidences a precipitate of β titanium containing chromium and columbium in solid solution. Beneath this overlay is a substrate region (diffusion zone) containing chromium and titanium in solid solution.

Siliconizing of the Cr-Ti coating results in the diffusion of silicon completely through the overlay portion of the Cr-Ti coating and into the substrate diffusion zone. The as-formed Cr-Ti-Si coating is basically a disilicide coating, containing composition gradients of chromium, titanium and columbium across the disilicide region. This region can be symbolized as $(Cr,Ti,Cb...)Si_2$. Two lower silicide bands which may be symbolized $(Cr,Ti,Cb...)_3(Si,W)_2$ and $(Cr,Ti,Cb...)_5(Si,W)_3$ are observed beneath the disilicide region. A substrate diffusion zone beneath the lower silicides contains chromium, titanium and silicon in solid solution. The thickness of the Cr-Ti-Si coating generally ranges from 1.5-3.5 mils.

Exposure of the Cr-Ti-Si coating in air at one atmosphere, at temperatures up to 2300°F, is accompanied by a weight gain which is essentially parabolic in nature (for at least 200 hours). At 1800°F the protective oxide is essentially silica, containing considerable chromium and titanium either as independent oxides or in solid solution. Exposure of the Cr-Ti-Si coating in air at 2500°F and above results in an initial weight gain, followed by a significant weight loss for a considerable period of the exposure. At 2500°F the initially formed surface scale is essentially Cr_2O_3, with lesser quantities of the oxides of titanium and silicon. Continual exposure at 2500°F results in the rapid loss of chromium, either by chromium or chromium oxide vaporization, eventually leaving a scale consisting of the oxides SiO_2, TiO_2, and possibly the complex oxide $TiO_2 \cdot Cb_2O_5$. The remaining disilicide coating is continually depleted of chromium and titanium, and enriched in columbium, until the disilicide can no longer sustain the formation of the protective oxide system. The less oxidation resistant lower silicides (also columbium rich) continually grow in width during the elevated temperature exposure. As the exposure temperature increases above 2500°F the increased diffusion rates and accelerated loss of chromium correspondingly reduce the coating protective life.

Reduced pressure oxidation of the Cr-Ti-Si coating at 2500°F again resulted in the rapid loss of chromium from the coating, however, this evaporation was accompanied by the additional loss of silicon via SiO volatilization. The enhanced loss of coating elements by vaporization at the reduced pressures greatly accelerates the failure mechanism characteristic of the Cr-Ti-Si coating. Failure of the Cr-Ti-Si coating by a wear-out type mechanism is basically the result of three phenomena: (1) depletion of chromium from the disilicide and from the protective oxide system, (2) enrichment of the disilicide and the oxide scale with columbium and (3) depletion of coating elements from the substrate. The latter factor is associated with the increased susceptibility of the substrate to crack or fissure formation in the coating during thermal cycling.

5. SPRAY COATING PROCESS

The majority of the currently reliable or at least promising protective coatings for columbium and other refractory metals are formed on the refractory metal substrates by various pack cementation processes. However, pack processes do not easily lend themselves to coating large or complex refractory metal structures, thus there exists an obvious need for the development of much simplier protective coating techniques. The reliability and protective capabilities of the pack processed Cr-Ti-Si coating on columbium materials has been well demonstrated, therefore, it was one of the objectives of this program to investigate the formation of this protective alloy system on columbium by a spray diffusion technique. The concept explored in this effort did not involve sintering or melting of the sprayed deposit on the substrate surface, but rather entailed a vapor-solid interface reaction analogous to that realized in the pack type process. The spray-diffusion technique was, therefore, a pseudo-pack process with the sprayed bisque providing a thin envelope of pack material.

5.1 Procedure

The spray slurries consisted of mixtures of 85-89 w/o metal powders, 10 w/o polyisobutylene binder and 1-5 w/o halide activator, suspended in a sufficient quantity of toluol to attain a satisfactory spraying viscosity. Sheared test coupons (1/2" x 1/2" x 0.030") were (1) degreased in trichlorethylene, (2) abrasively tumbled to remove burrs and (3) chemically etched in an aqueous solution of HF, H_2SO_4 and HNO_3 acids. The coupons were subsequently sprayed with a desired slurry build-up, and then air dried to form a green bisque with adequate handling strength. Diffusion treating of the sprayed coupons was accomplished in an induction heated vacuum furnace normally employed in the pack coating process. The specimens were contained in a refractory metal retort partially sealed with a getter of 50Cr-50Ti alloy granules. Following the diffusion treatment the coupons were brushed to remove the loosely adhering sintered bisque.

83

The Cr-Ti and silicon coating cycles were investigated independently, and an attempt was also made to form the Cr-Ti-Si coating in one diffusion cycle. The results of these individual approaches will be presented independently in the subsequent subsections. The process variables which were given consideration in the development of the slurry diffusion process were as follows:

(a) Substrate (columbium alloy)   (f) Diffusion environment

(b) Slurry metal composition (Cr,Ti,Si) (g) Diffusion temperature

(c) Metal particle size   (h) Diffusion time

(d) Activator quantity   (i) Specimen support media

(e) Bisque thickness   (j) Spraying sequence

The criteria for evaluating the slurry processed Cr-Ti-Si coatings were the microstructures and the protective properties of analogous pack processed coatings.

5.2 Cr-Ti Coating Cycle

In the first series of experiments with the slurry process a full factorial analysis was made of the following variables:

(a) Substrates - D-43 alloy
                  B-66 alloy

(b) Metal powder compositions - weight percent

            50Cr-50Ti (prealloyed)
            60Cr-40Ti (prealloyed)

(c) Metal particle size - -230 mesh
                           -325 mesh

(d) Activator - 0.5 w/o NaF
                 2.0 w/o NaF

(e) Diffusion environments - Continuous furnace evacuation -

            10^{-2} mm pressure

            Argon partial pressure - 150 mm

84

The slurries were prepared with prealloyed Cr-Ti powders identical to those employed in the vacuum pack coating process. A nominal bisque thickness of 5 mils was spray deposited on the test coupons. The coupons were supported in a bed of -50+80 mesh 60Cr-40Ti alloy powder, in a partially sealed retort. In all cases the diffusion treatment involved 6 hours at 2300°F with either: (1) continuous furnace evacuation at an average pressure of 10^{-2} mm, or (2) initial furnace evacuation followed by blanking-off and backfilling the furnace with argon to a system pressure of 150 mm. Metallographic specimens were prepared representing each of the above listed variables, and measurements were made of the coating overlay and diffusion zone thicknesses. These data are presented in Table 11 and shown graphically in Figure 49.

It is evident from the scatter diagram in Figure 49 that diffusion environment was the most influential variable of those evaluated. A considerably thinner overlay resulted from diffusion treating in a dynamic vacuum, as opposed to the static partial pressure of argon. This was apparently a consequence of the relatively faster removal of the volatilized halide from the thin bisque in a dynamic vacuum. Although the overlay portion of the Cr-Ti coatings were generally comparable both in thickness and in appearance to those obtained by pack processing, the substrate diffusion zone characteristic of the pack Cr-Ti-Si coating was absent. A microstructural comparison of slurry and pack processed Cr-Ti coatings is shown in Figure 50. Only in areas where the sprayed surface was in close proximity to the 60Cr-40Ti support material was there evidence of a titanium (chromium) enriched diffusion zone beneath the Laves phase.

Since the use of the 60Cr-40Ti alloy support material resulted in coatings which were both non-uniform and misleading with regard to microstructural characteristics, a brief investigation was made of two other support media: (1) Al_2O_3 granules and (2) columbium and tantalum sheet metal fixtures. It was found that Cr-Ti coatings formed on specimens supported in the refractory metal fixture were uniform, and of comparable overlay thickness to those supported in the 60Cr-40Ti powder. Adverse effects were experienced as a result of supporting the Cr-Ti sprayed coupons in Al_2O_3 granules. For otherwise comparable processing conditions, support in the refractory oxide reduced the Cr-Ti alloy overlay thickness to nearly one-half that obtained with the refractory metal fixture. The detrimental effect of the oxide granules was apparently associated with either absorption of the halide activated metal species or reaction of the oxide with the halide activator. Based on these data, in all subsequent work with the spray-diffusion process tantalum or columbium sheet metal fixtures were employed to support the sprayed test specimens.

In the second series of experiments a brief evaluation was made of the influence of diffusion temperature on Cr-Ti coatings formed by the spray-diffusion process. A single run was made at 2200°F employing 50Cr-50Ti and 60Cr-40Ti alloy slurries and various activator quantities. The metallographic data are compared in Table 12, with data representative of Cr-Ti coatings formed by diffusion treating at 2300°F. The overlay thickness obtained at

85

TABLE 11

Metallographic Measurements for Cr-Ti Coatings Formed on
Columbium Alloys by the Spray-Diffusion Process-
6 Hours - 2300°F

Slurry Composition w/o	Diffusion Environment	Metal Particle Size	Overlay Thickness - Mils(a)			
			D-43		B-66	
			0.5 w/o NaF	2 w/o NaF	0.5 w/o NaF	2 w/o NaF
50Cr-50Ti	10^{-2} mm	-230	0.3-0.4	0.4-0.5	0.3-0.7	0.5-0.7
		-325	0.3-0.4	0.4-0.5	0.3-0.7	0.5-0.7
50Cr-50Ti	Argon 150 mm(b)	-230	0.6-0.8	0.6-0.8	0.6-0.9	0-0.6
		-325	0.6-0.8	0.6-0.8	0.6-0.8	0-0.3
60Cr-40Ti	10^{-2} mm	-230	0.2-0.4	0.3-0.4	0.4-0.7	0.4-0.6
		-325	0.3-0.4	0.3-0.4	0.3-0.5	0.4-0.6
60Cr-40Ti	Argon 150 mm	-230	0.7-0.8	0.6-0.8	0.6-0.8	0.7-1.0
		-325	0.7-0.8	0.6-0.8	0.4-0.6	0.6-0.8

(a) Diffusion Zone Nil - All Specimens

(b) Initial furnace evacuation followed by argon backfill to 150 mm pressure
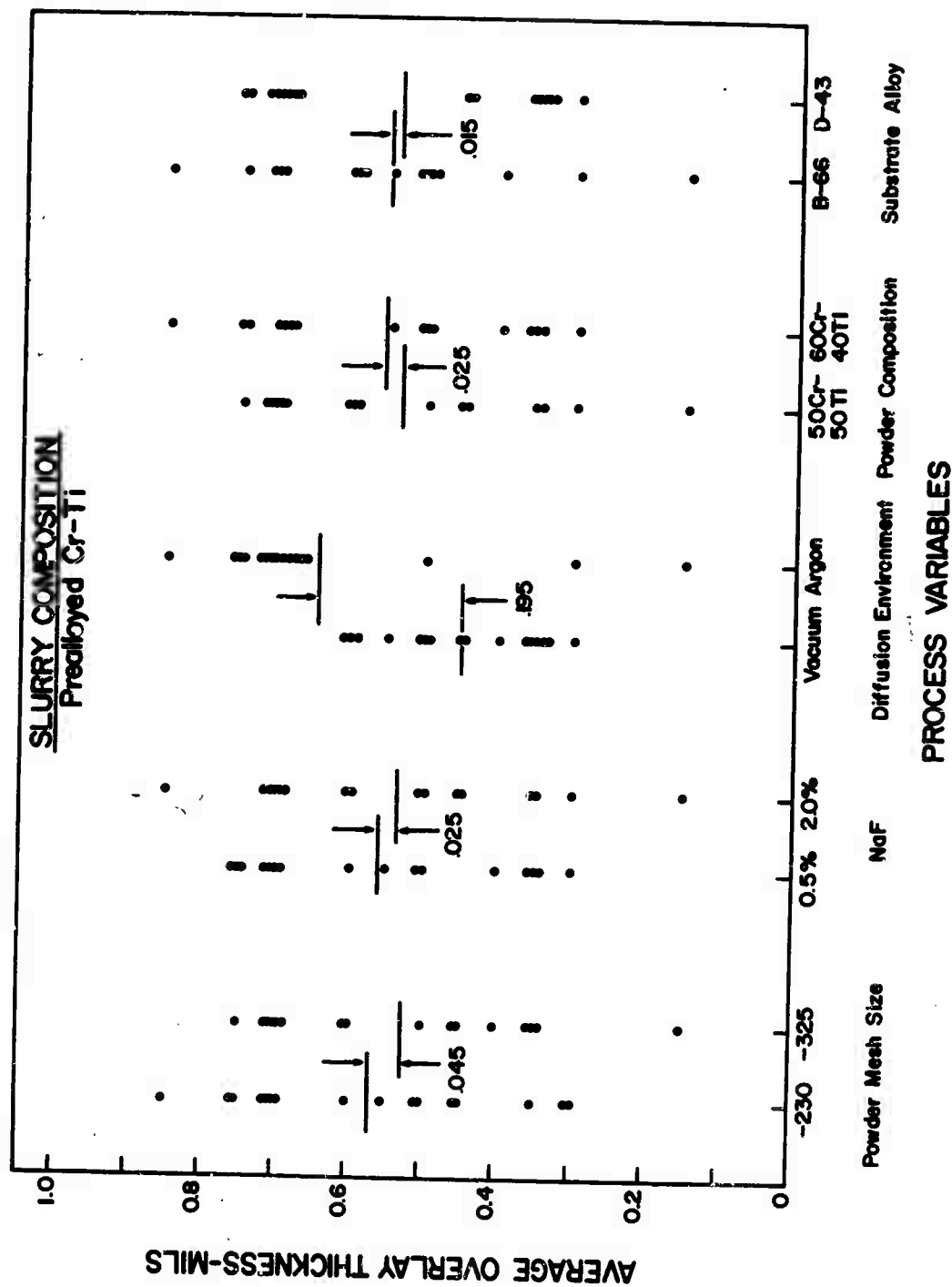
Figure 49 Influence of Process Variables on the Overlay Thickness of Sprayed and Diffused Cr-Ti Alloy Coatings - Process Cycle - 6 Hours

Overlay

Diffusion Zone

Pack   Cr-Ti

Overlay

Spray   Cr-Ti
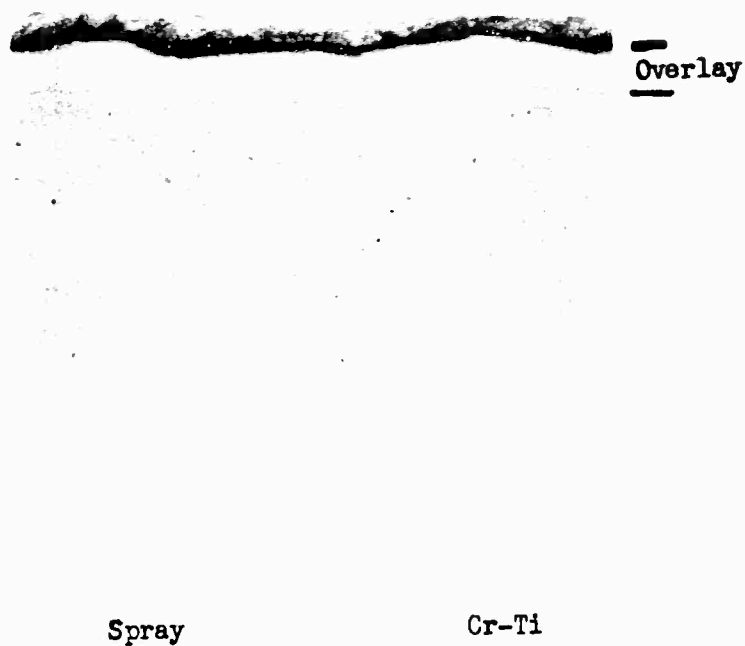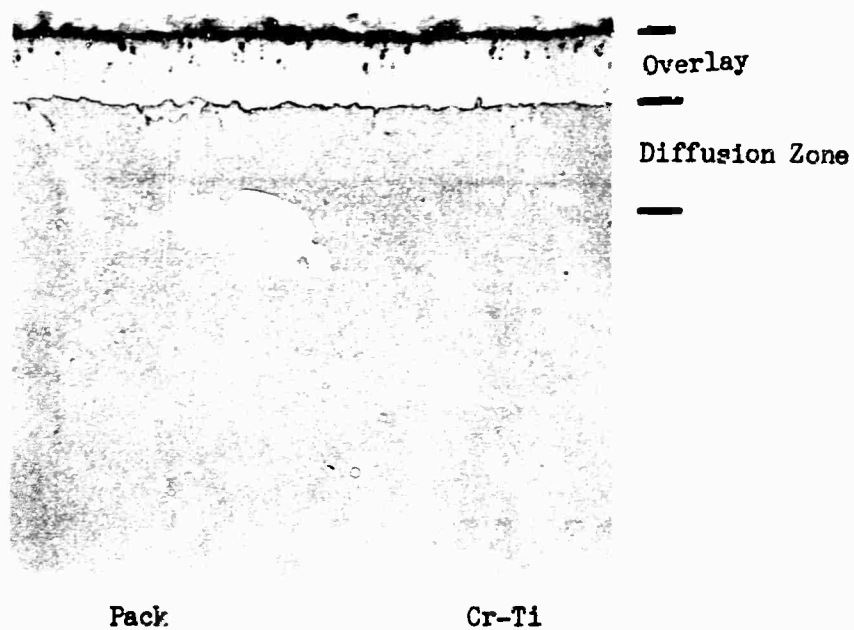
Figure 50 Comparision of Pack and Spray Processed Cr-Ti Coatings on
B-66 Alloy   500X

TABLE 12

Metallographic Results for Cr-Ti Coatings Formed on
B-66 and D-43 Alloys Using the Spray-Diffusion Technique[a]

Substrate	Slurry Metal Composition-w/o	Activator w/o NaF	Overlay Thickness - Mils[b]	
			2200°F	2300°F
B-66	50Cr-50Ti	0.5	0.4	0.6-0.9
		1.0	0.2-0.4	-
		2.0	0.4	0.6
B-66	60Cr-40Ti	0.5	0.4	0.6-0.8
		1.0	0.4	-
		2.0	0.3-0.4	0.7-1.0
D-43	50Cr-50Ti	0.5	0.4	0.6-0.8
		1.0	0.4	-
		2.0	0.4	0.6-0.8
D-43	60Cr-40Ti	0.5	0.4	0.7-0.8
		1.0	0.3-0.4	-
		2.0	0.3-0.4	0.7-0.8

(a) Processing Conditions - 6 Hours - 2200 or 2300°F
     150 mm Argon
     Nominal bisque thickness - 5 mils

(b) Diffusion Zone Nil - All conditions

89

2200°F was about one-half that formed in a comparable time (6 hours) at
2300°F, and again there was no metallographic evidence of the titanium
enriched diffusion zone beneath the overlay. Neither slurry metal compo-
sition or activator quantity significantly influenced the overlay thickness.
Although a thinner coating was formed at 2200°F, the alloy layer was
sufficiently thick, considering the relatively short coating time, to
warrant further studies at this lower diffusion temperature.

A third series of experiments were conducted to investigate the
influence of a shorter diffusion time (3 hours), and various levels of
three other variables which were as yet unestablished: (1) slurry metal
composition, (2) activator quantity and (3) bisque thickness. These data
are tabulated in Table 13 and are also plotted as a scatter diagram in
Figure 51. Slightly thicker Cr-Ti alloy coatings were again formed with
the higher chromium slurry composition, and again, neither composition
produced sufficient titanium in the vapor phase to establish a metallogra-
phically evident titanium enriched region beneath the coating overlay.
The quantity of halide activator in the slurry, in the range 0.5-5.0 w/o,
also exhibited little influence on the coating overlay thickness or diffusion
zone.

Bisque thickness was the most significant parameter varied in this
run. Increasing the sprayed bisque thickness from 2 to 10 mils produced
a marked increase in the average Cr-Ti overlay thickness, whereas further
increase of the bisque thickness to 20 mils was of little additional
benefit.

It was evident at this point in the program that the titanium deficiency
in the slurry processed Cr-Ti coatings was the major problem to be pursued.
Variation of the bisque composition was considered to be the most logical
approach to obtaining the desired coating microstructure, and the remaining
variables were held constant at the following levels:

        (a)   temperature - 2300°F

        (b)   diffusion time - 6 hours

        (c)   system pressure - 150 mm argon

        (d)   activator - 1.0-2.0% NaF

        (e)   bisque thickness - 10 mils mininum

        (f)   specimen support media - refractory

            metal fixture

90

TABLE 13

Metallographic Results for Cr-Ti Coatings Formed on B-66 and D-43 Alloys Using the Spray-Diffusion Technique[a]

Substrate	Slurry Metal Composition w/o	Nominal Bisque Thickness Mils	Overlay Thickness - Mils[b]			
			0.5% NaF	1.0% NaF	2.0% NaF	5.0% NaF
B-66	50Cr-50Ti	2	0.2-0.4	-	0.2-0.4	-
		5	0.2	0.2	0.2-0.3	0.2-0.6
		10	0.7	-	0.5	-
		20	0.5-0.6	-	-	0.4-0.5
B-66	60Cr-40Ti	2	-	-	-	-
		5	0.4	0.3-0.4	0.6-0.7	0.2-0.6
		10	-	-	-	-
		20	0.5-0.6	-	-	0.4-0.6
D-43	50Cr-50Ti	2	0.2-0.6	-	0.4-0.6	-
		5	0.5-0.6	0.4-0.5	0.4	0.3-0.4
		10	0.6	-	0.6	-
		20	0.6-0.7	-	-	0.6-0.7
D-43	60Cr-40Ti	2	-	-	-	-
		5	0.6-0.7	0.5-0.7	0.6	0.3-0.5
		10	-	-	-	-
		20	0.6-0.7	-	-	0.5-0.6

(a) Processing Conditions: 3 hours - 2300°F
150 mm argon

(b) Diffusion Zone - Nil - All conditions

91
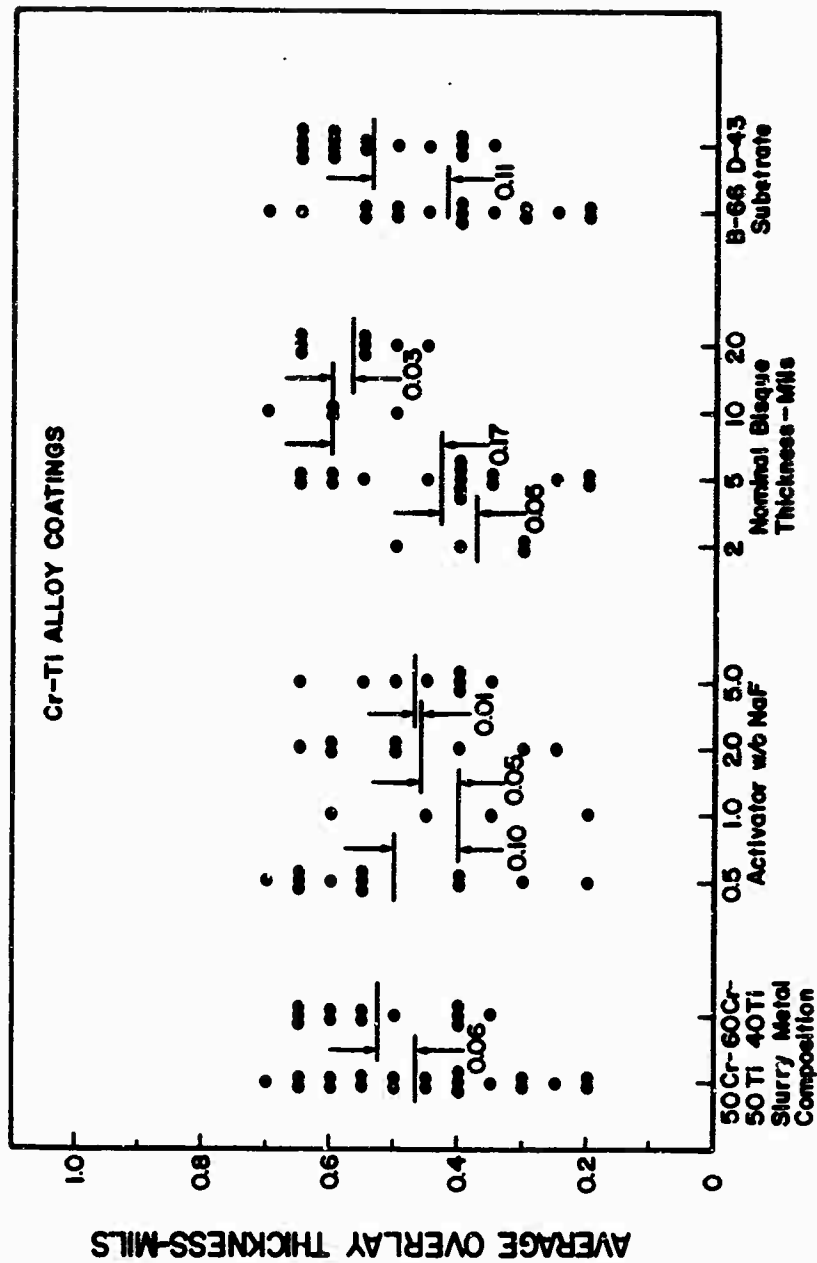
Figure 51 Influence of Process Variables on Overlay Thickness of Sprayed and
Diffused Cr-Ti Alloy Coatings on B-66 and D-43 Alloys - Process
Cycle - 3 Hours

92

Two factors are apparent which may have been contributing to the differences in coating behavior of the sprayed bisques and granular packs. The volatilized activator and vaporized coating element species are removed much more readily from the thin bisque than from the massive pack in a dynamic system. The efficient transfer of titanium from the pack or slurry metal is more dependent upon the residence time of the activator than is the transfer of chromium, hence, the titanium deficiency from the slurry bisque. Also, the residual gases in the evacuated system are gettered by the pack or bisque materials during the coating cycle. Titanium is the primary gettering element and substantial contamination of this species in the thin bisque would reduce its transport efficiency. To alleviate this problem slurries were prepared with titanium concentrations exceeding that provided by the 50Cr-50Ti prealloyed composition, and a variety of spray procedures were employed with these slurries.

The compositions studied were as follows (weight percent):

(a)	50Cr-50Ti	Prealloyed
(b)	30Cr-70Ti	Prealloyed
(c)	50 (50Cr-50Ti) + 50Ti	Mixture
(d)	80 (50Cr-50Ti) + 20Ti	Mixture
(e)	85 (50Cr-50Ti) + 15Ti	Mixture
(f)	90 (50Cr-50Ti) + 10Ti	Mixture
(g)	95 (50Cr-50Ti) + 5Ti	Mixture
(h)	100Ti	-

Three application techniques were investigated:

(1) A single spray consisting of 10 mil thick (minimum) bisques of compositions (a) through (g)

(2) A duplex spray consisting of 1-2 mils of pure titanium (composition(h)) oversprayed with 10 mils of compositions (a) or (b)

(3) A duplex spray consisting of 10 mils of compositions (a) or (b) oversprayed with 1-2 mils of pure titanium

These combinations were diffusion treated for 6 hours at 2300°F in 150 mm of argon. The substrate material for all of this work was B-66 alloy.

Increasing the titanium content of the prealloyed metal compositions from 50 to 70 w/o apparently provided no appreciable increase in the titanium content of the coating vapor phase. This was indicated by the absence of a metallographically evident diffusion zone in the resulting coating microstructures (Figure 52).

93
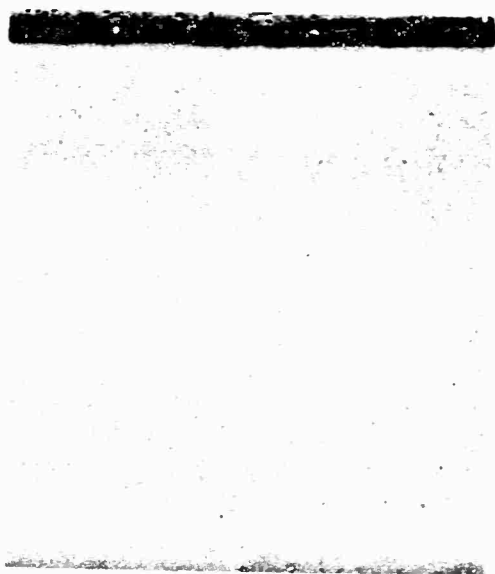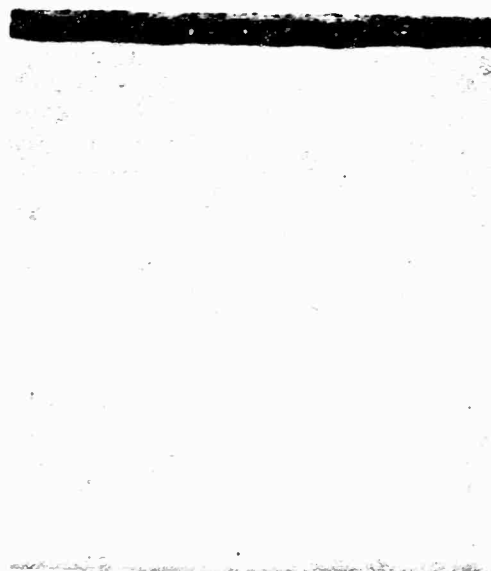
50Cr-50Ti   30Cr-70Ti

Prealloyed Powders (w/o)
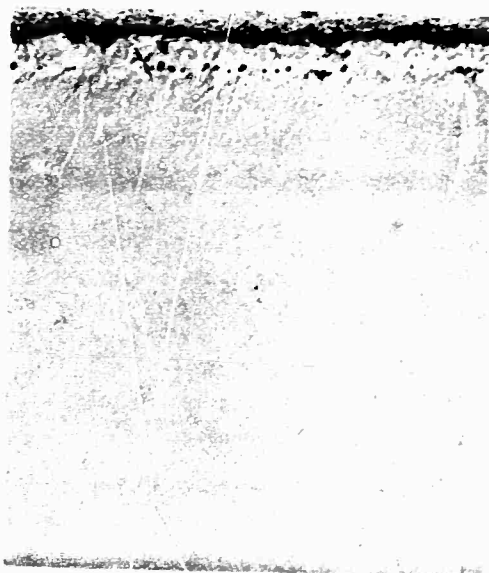
Bisque - 1 Mil Pure Ti   Bisque - 10 Mils 50Cr-50Ti
Over 10 Mils 50Cr-50Ti   Over 1 Mil Pure Ti

Duplex Sprays

Figure 52   Cr-Ti Coatings Formed on B-66 Alloy by the Spray-Diffusion
            Technique - 6 Hours - 2300°F   250X

94

Both duplex spray techniques were equally unsuccessful in producing Cr-Ti coatings analogous to pack processed coatings. The thin, pure titanium bisque adjacent to the substrate surface shielded the surface from the chromium vapors, resulting in the formation of only a columbium-titanium solid solution (diffusion zone) on the substrate surface. On the other hand, overspraying the Cr-Ti alloy bisque with pure titanium produced an excess of titanium in the vapor phase, as evidenced by the pronounced diffusion zone and excessive interdiffusion of chromium and columbium (Figure 52).

The alternate technique employed in attempting to optimize the Cr-Ti bisque composition involved mechanically mixing pure titanium with the prealloyed Cr-Ti powders. Slurries prepared from these mixtures ranged in composition from 5 to 50 w/o pure titanium mixed with prealloyed 50Cr-50Ti (compositions (c) through (g)). Photomicrographs of several representative coatings formed from these compositions are shown in Figure 53. Cr-Ti coatings produced from compositions containing more than 10 w/o titanium evidenced an excess of titanium, gross porosity and considerable non-uniformity in coating microstructure. The 5 w/o titanium mixture was too lean in titanium as evidenced by the absence of a titanium enriched diffusion zone. The 10 w/o titanium composition produced Cr-Ti coatings bearing the closest microstructural resemblance to the pack type coatings, but still comparatively deficient in titanium.

Mechanically mixing the prealloyed Cr-Ti powders with pure titanium appeared to be the most promising technique for Cr-Ti slurry preparation. However, an extremely important factor in this procedure was the attainment of slurry (bisque) homogeneity. For example, in the early development of the pack process it was found that mechanical mixtures of relatively large chromium and titanium granules (-8 +30 mesh) produced very heterogeneous Cr-Ti coatings, owing to the large surface area of the metal particles. Mechanical mixtures of the fine metal particles (-250 mesh) in the sprayed bisques were satisfactory, on the other hand, providing segregation of the metal powders did not occur during spraying.

From this latter investigation of slurry composition, the 90 w/o (50Cr-50Ti) + 10 w/o Ti slurry mixture displayed the most promise for formation of the Cr-Ti coating. The use of a prealloyed Cr-Ti powder in this slurry was somewhat undesirable from an economic point, and a final series of coating runs were conducted to explore the use of pure chromium and titanium as the slurry metal constituents.

Four pure metal slurry compositions were employed (weight percent):

(a) 60Cr-40Ti
(b) 70Cr-30Ti
(c) 80Cr-20Ti
(d) 90Cr-10Ti

95
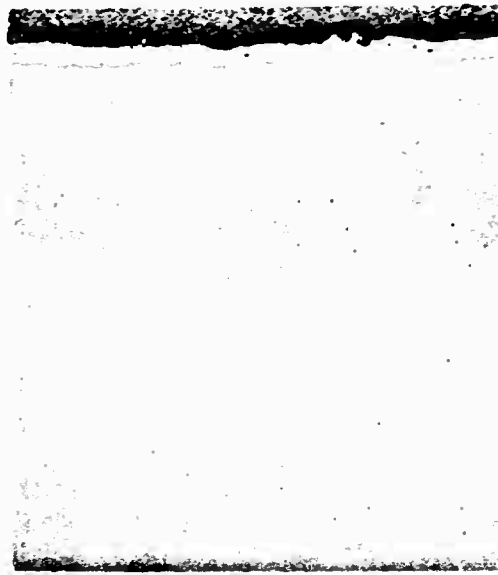
95 (50Cr-50Ti) + 5Ti   90 (50Cr-50Ti) + 10 Ti
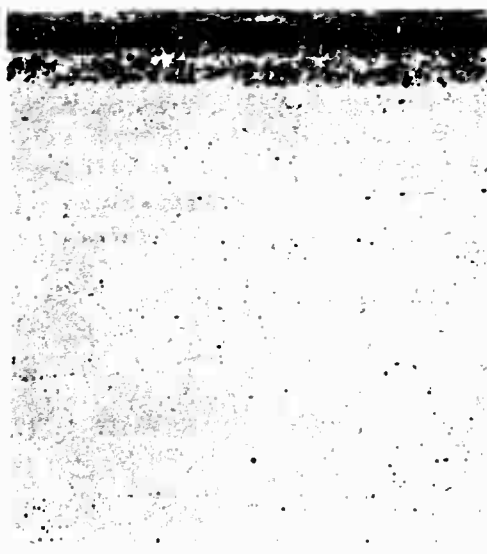
85 (50Cr-50Ti) + 15 Ti   80 (50Cr-50Ti) + 20 Ti

Figure 53   Cr-Ti Coatings Formed on B-66 Alloy by the Spray-Diffusion Technique
Using a Mechanical Mixture of Prealloyed 50Cr-50Ti and Pure Titanium
Powders (w/o), 6 Hours - 2300°F   250X

with the mixture of prealloyed 50Cr-50Ti and pure titanium powders included as the control composition. Both D-43 and B-66 alloy coupons were sprayed with these compositions, and four independent diffusion treatments were performed, each involving 8 hours at 2300°F in 150 mm of argon. Figure 54 presents photomicrographs showing the Cr-Ti coatings formed on D-43 alloy, employing the four pure metal slurry compositions. The slurries containing 30-40 w/o Ti were too rich in titanium, as evidenced by the excessive penetration of chromium and titanium into the substrate surface and the absence of a continuous Laves phase overlay. Each of the remaining three compositions (10-20 w/o titanium) produced coatings with continuous intermetallic overlays, however, the 90 (50Cr-50Ti) + 10Ti composition provided both a more uniformly thick overlay coating and a more apparent diffusion region in the adjacent substrate. As discussed in Section 4, the optimum microstructure for the Cr-Ti coating, based on oxidation properties of the Cr-Ti-Si system, consists of a continuous Laves phase overlay (0.8-1.0 mil) and a metallographically evident diffusion region, as shown in Figure 50.

Based on these metallographic results the slurry mixture containing the 90 w/o prealloyed Cr-Ti powder and 10 w/o pure titanium was selected as the tentatively optimum composition for the slurry-diffusion formation of the Cr-Ti coating. Undoubtedly the formation of an equivalent or superior Cr-Ti coating can be achieved with a slurry composed of pure chromium and pure titanium constituents rather than the prealloyed powder plus pure titanium metal; however, the required parameters were not established in this program.

5.3 Siliconizing Cycle

Much of the development work with the siliconizing cycle was conducted after certain processing variable levels had been established in investigating the Cr-Ti coating cycle. These variables were:

(a) Diffusion environment - 150 mm argon

(b) Metal particle size - -250 mesh

(c) Specimen support media - refractory metal

The slurry metal composition was 100 w/o silicon.

In the initial experiments with the silconizing treatment the following process variables were investigated: (a) diffusion temperature - 1900, 2000, and 2100°F (3 hours), (b) bisque thickness - 2-10 mils and (c) activator quantity - 0.5-2.0 w/o NaF. Silicide coatings were formed on both uncoated and Cr-Ti coated D-43 and B-66 alloy coupons, employing random combinations of various levels of the above variables. The objective in this approach was to quickly establish which were the more significant process variables and what was the general direction for optimization. The results from these runs are given in Tables 14 and 15, and the data are plotted in scatter diagrams in Figure 55.

97

70Cr-30Ti

80Cr-20Ti
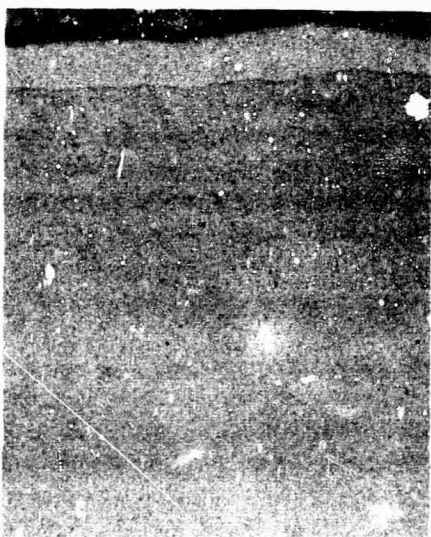
90Cr-10Ti
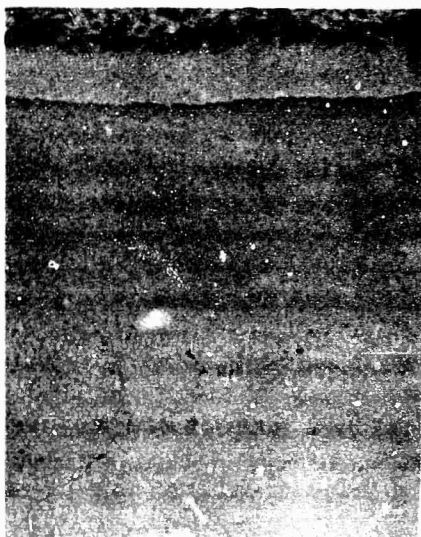
90(50Cr-50Ti)-10Ti

Figure 54 Microstructures of Cr-Ti Coatings Formed on D-43 by the Spray-
         Diffusion Technique   500X

TABLE 14

Metallographic Results for Coatings Formed on B-66 Alloy Utilizing the Spray-Diffusion Siliconizing Technique(a)

Processing Conditions(b)		Initial Surface Condition	Nominal Bisque Thickness Mils	Overlay Coating Thickness-Mils		
Time Hrs.	Temperature °F			0.5% NaF	1.0% NaF	2.0% NaF
3	1900	Uncoated	2.0	0.8-1.4	-	0.8-0.9
			5.0	1.6-1.8	1.4-1.8	1.6-1.9
			10.0	1.6-1.8	-	1.4-.8
3	1900	Cr-Ti(c) Coated	5.0	1.2-1.6	1.2-2.0	2..4.6
3	2000	Uncoated	2.0	0.8-1.2	-	0.6-0.8
			5.0	1.2-2.0	1.4-2.0	1.4-1.8
			10.0	2.0-2.2	-	2.0-2.2
3	2000	Cr-Ti Coated	5.0	2.0-2.6	1.2-2.6	2.0-2.6
3	2100	Uncoated	2.0	1.4-2.4	-	0.6-0.8
			5.0	1.6-2.4	1.4-2.0	1.4-2.0
			10.0	2.4-3.4	-	1.8-2.2
3	2100	Cr-Ti Coated	5.0	1.2-1.6	1.2-3.2	2.2-2.4

(a) Slurry Metal Composition - 100 w/o Si

(b) System Pressure - 150 mm argon

(c) Cr-Ti Coating - Pack processed - 60Cr-40Ti
           8 hours - 2300°F - 1.5 mm
           Overlay thickness - 0.7-0.8 mils

99

TABLE 15

Metallographic Results for Coatings Formed on D-43 Alloy Utilizing the Spray-Diffusion Siliconizing Technique[a]

Processing Conditions[b]		Initial Surface Condition	Overlay Coating Thickness-Mils		
Time Hrs.	Temperature °F		0.5% NaF	1.0% NaF	2.0% NaF
3	1900	Uncoated	1.0-1.4	1.2-1.3	1.2-1.3
		Cr-Ti Coated[c]	1.6-2.4	2.0-2.4	2.0-2.4
3	2000	Uncoated	1.4-1.8	1.2-1.6	1.2-1.8
		Cr-Ti Coated	2.2-2.6	1.4-2.4	2.2-2.6
3	2100	Uncoated	1.0-1.5	1.6-1.8	1.6-2.4
		Cr-Ti Coated	2.2-2.4	2.2-3.2	2.6-3.0

(a) Slurry Metal Composition - 100 w/o Si

(b) System Pressure - 150 mm argon
Nominal Bisque Thickness - 5.0 mils

(c) Cr-Ti Coating - Pack processed - 60Cr-40Ti
8 hours - 2300°F - 1.5 mm
Overlay thickness - 0.7-0.8 mils
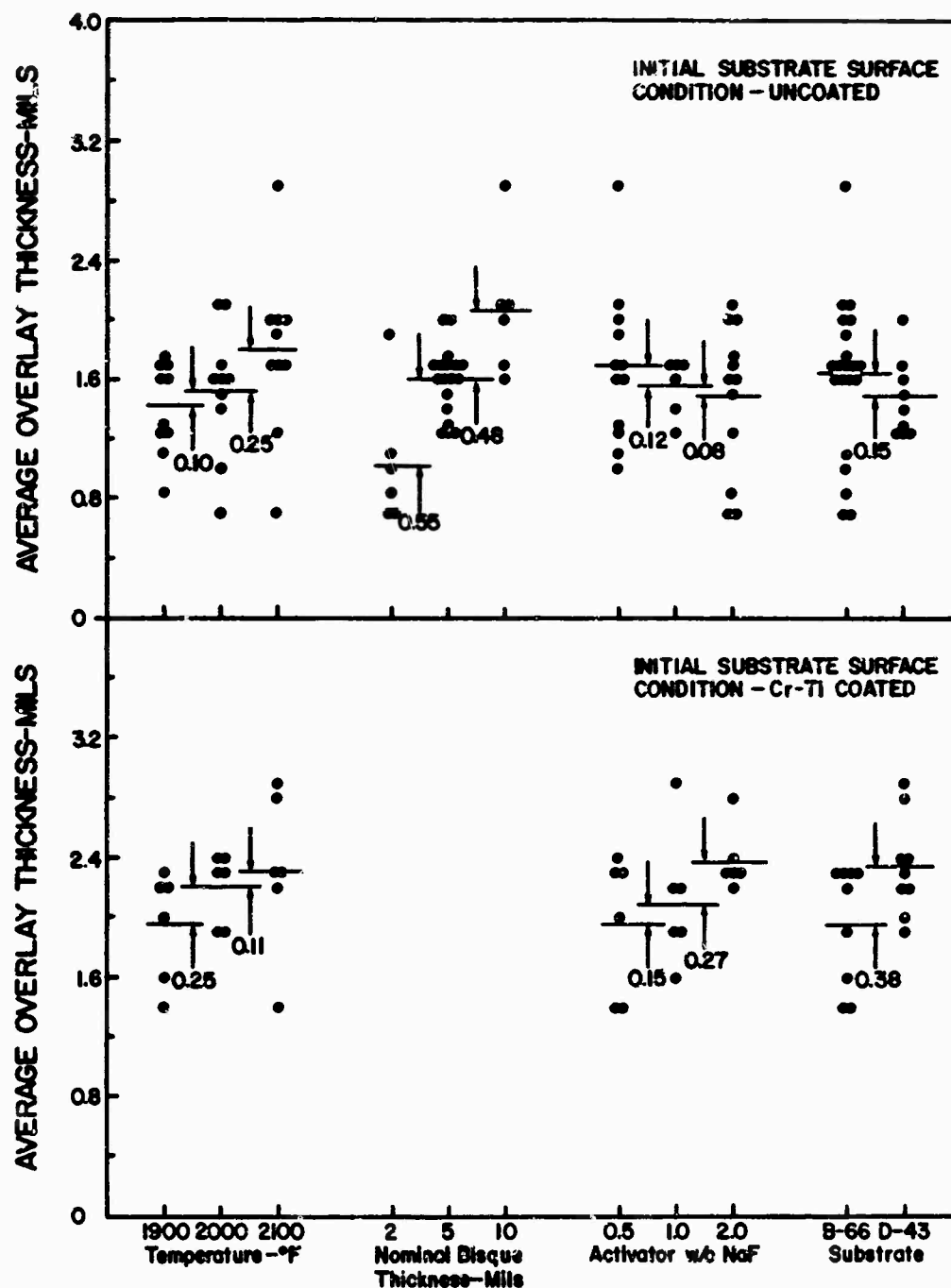
Figure 55   Influence of Process Variables on Coating Thickness of Sprayed and
Diffused Si and Cr-Ti-Si Coatings on B-66 and D-43 Alloys - Slurry
Composition - 100 w/o Si

101

The effect of diffusion temperature was reasonably consistent for all combinations of variables, evidencing a general increase in coating thickness with increasing temperature. Bisque thickness was evaluated only on the uncoated B-66 alloy and was a markedly significant variable. A 100% increase in average coating thickness was realized by increasing the bisque thickness from 2 to 10 mils. Based on these results, and those obtained with the spray diffused Cr-Ti coatings, a minimum bisque thickness of 10 mils was deemed adequate for attaining coating uniformity. Unfortunately, this series of experiments was run concurrently with the investigation of the Cr-Ti cycle, and a nominal bisque thickness of 5 mils was employed. This thinner bisque undoubtedly accounts in part for the noticeable scatter in the data.

Activator quantity had little influence on the thickness of the silicide coatings formed on the uncoated columbium substrates, whereas in siliconizing the Cr-Ti coated coupons a moderate increase in Cr-Ti-Si coating thickness was noted with increasing activator quantity. The reason for this difference was not apparent.

A second series of siliconizing experiments were conducted to establish the processing parameters from which predictable and uniform coating thicknesses could be obtained. In order to expedite the preparation of Cr-Ti coated coupons for this work, a group of B-66 alloy specimens were Cr-Ti coated using the vacuum pack process. A slurry of pure silicon was employed in this siliconizing study, and specimens were prepared for both metallographic and cyclic oxidation evaluation. Diffusion treatments of 1, 3 and 5 hours at 1900, 2000 and 2100°F were performed, and the metallographic data are presented in Table 16 and shown graphically in Figure 56. With increasing silicon diffusion time (1 to 5 hours), the average Cr-Ti-Si coating thickness increased by a factor of approximately three at 1900°F (1.0 to 3.0 mils), and by a factor of approximately two at both 2000°F (2.0 to 3.8 mils) and 2100°F (2.4 to 4.2 mils). Figure 57 presents photomicrographs showing this time increase in coating thickness. Note that the lighter etching region near the coating surface remained essentially constant in thickness, and the coating grew by expansion of the darker etching region adjacent to the substrate. This dark layer expanded by the diffusion of silicon (Cr,Ti) into the original diffusion zone beneath the Cr-Ti overlay coating. Increasing the diffusion temperature at a fixed time produced a similar increase in coating thickness, and these microstructural changes are shown in Figure 58.

Oxidation studies were conducted with specimens coated under each of these different siliconizing conditions to evaluate the influence of processing temperature on the coating protective life. At 1800°F coatings processed under all conditions were equally protective (100%) within the time limit of the oxidation test (104 hours). At 2500°F the protective life of the Cr-Ti-Si coatings increased with increasing coating thickness (53-150 hours), and there were no premature coating failures. For coatings of approximately comparable silicide overlay thickness, siliconizing at 2000 or 2100°F produced coatings slightly superior to those formed at 1900°F.

102

TABLE 16

Metallographic and Cyclic Oxidation Test Results from Investigation of Spray Processing Parameters for Siliconizing Cycle

Processing Conditions[a]		Cr-Ti-Si Coating[b]	Protective Life - Hours	
Time Hrs.	Temperature °F	Thickness - Mils	1800°F	2500°F
1	1900	1.2-1.3	>104(4) [c]	53,55,72,72
3		2.2-2.5	>104(4)	94,94,96,120
5		2.7-3.0	>104(4)	96,96,96,128
1	2000	1.9-2.0	>104(4)	53,72,96,120
3		3.0-3.4	>104(4)	120,120,120,128
5		3.6-4.0	>104(4)	120,120,128,128
1	2100	2.4-2.8	>104(4)	96,120,120,128
3		4.0-4.3	>104(4)	>150(4)
5		3.6-4.4	>104(4)	72,128,128,128

(a) Pressure - 150 mm argon
    Activator - 1.0% NaF

(b) Base Material - Cr-Ti coated B-66 alloy
    Cr-Ti coating thickness - 0.8-1.0 mils
    Diffusion zone - 1.0-1.2 mils

(c) Denotes number of replicate coupons
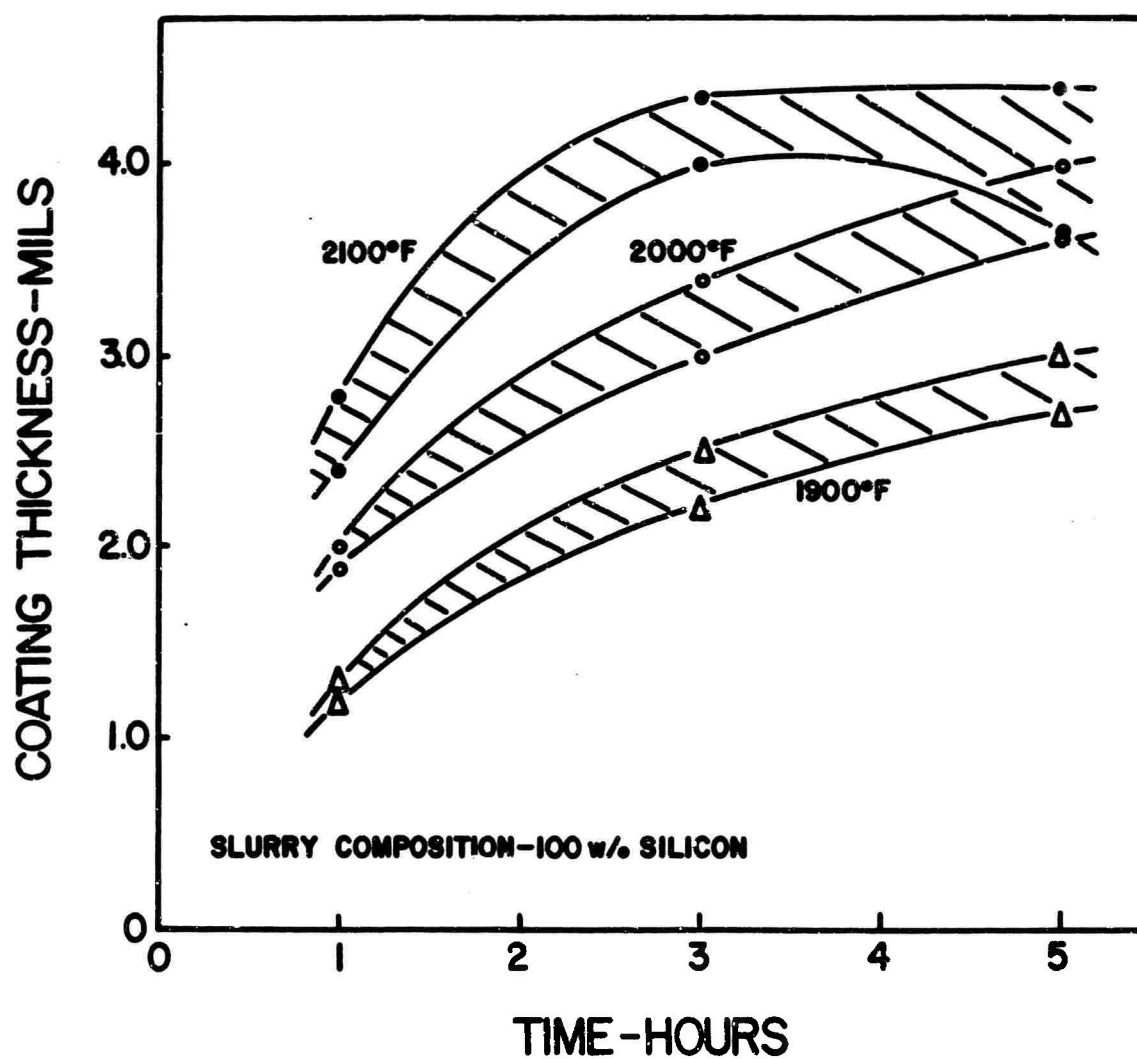
Figure 56   Influence of Siliconizing Time and Temperature on Thickness
            of Spray-Diffused Cr-Ti-Si Coatings on B-66 Alloy

104
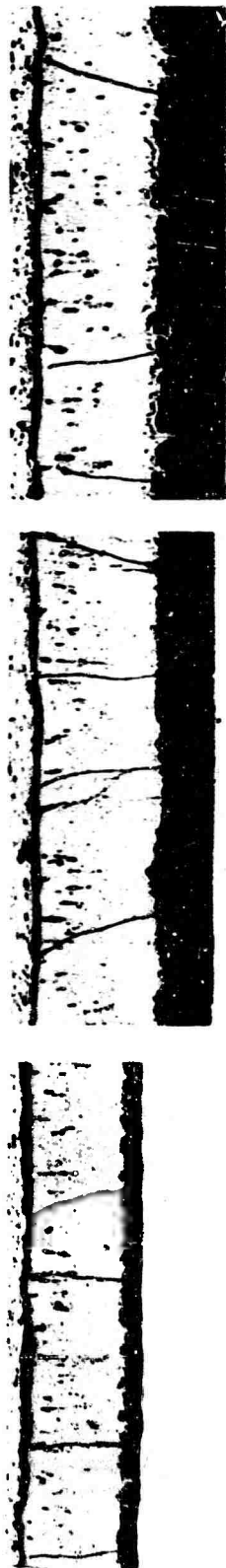
1 Hour - 2100°F

3 Hours - 2100°F

5 Hours - 2100°F

Figure 57 Influence of Siliconizing Time at 2100°F on Microstructures of Cr-Ti-Si Coatings Formed on B-66 Alloy by the Spray-Diffusion Process 250X

5 Hours – 1900° F

5 Hours – 2000° F

5 Hours – 2100° F

Figure 58   Influence of Siliconizing Temperature on Microstructures of Cr-Ti-Si Coatings Formed on B-66 Alloy by the Spray-Diffusion Process   250X

106

Based on these studies of the slurry siliconizing treatment, the following process parameters were considered tentatively optimum for the formation of 3.0-3.5 mil Cr-Ti-Si coatings on Cr-Ti coated columbium substrates:

(a) Slurry metal composition - 100 w/o silicon

(b) Activator quantity - 1.0 w/o NaF

(c) Bisque thickness - 10 mils minimum

(d) Diffusion environment - 150 mm argon

(e) Diffusion temperature - 2000°F

(f) Diffusion time - 3 hours

5.4 Single Cycle Formation of the Cr-Ti-Si Coating

In conjunction with conducting the various Cr-Ti and silicon slurry coating experiments, a cursory study was made of the feasibility of forming a Cr-Ti-Si coating by a single cycle process. Two techniques were employed in the spray deposition of the Cr-Ti-Si bisque: (1) a duplex bisque consisting of an initial Cr-Ti slurry deposit oversprayed with silicon and (2) a co-sprayed slurry mixture composed of prealloyed Cr-Ti and silicon powders. Both 50Cr-50Ti and 60Cr-40Ti alloys powders were utilized in these experiments.

Bisques were spray deposited on both B-66 and D-43 alloy coupons by these techniques. The diffusion treatments were accomplished in 6 hours at 2300°F, in both vacuum (10^{-2} mm) and in an argon backfilled furnace (150 mm). The metallographic data determined from the resulting coatings are given in Table 17. Techniques A and B, involving initially spraying a Cr-Ti bisque and then overspraying with silicon prior to heat treating, did not appear to be a feasible means of forming the Cr-Ti-Si coating on columbium. As shown in Table 17 the coatings thus formed were extremely non-uniform in thickness, and the diffusion of titanium into the substrate was nil. In some areas the coating consisted of only a Cr-Ti alloy layer, whereas in other areas only a silicide layer was formed.

Coatings C and D represent an alternate attempt to form the Cr-Ti-Si coating in a single step diffusion cycle. Again the coatings formed were quite non-uniform in thickness and there was little evidence of titanium diffusion into the columbium substrate. Also, dilution of the silicon slurry with the Cr-Ti alloy powder significantly reduced the rate of silicide coating formation, based on a comparison with silicide coatings formed at lower temperatures utilizing pure silicon slurries.

Figure 59 shows photomicrographs of typical coatings formed on a columbium alloy by this technique. The microstructural appearance of the coating is that of a straight silicide, and there is no evidence that signifi-

107

TABLE 17

Metallographic Results of Silicide Coatings Formed on Columbium Alloys by Single Cycle Diffusion of Cr-Ti-Si Bisques

Spray[2] Coating	Metal Particle Size	Diffusion Environment	Overlay Thickness - Mils			
			D-43		B-66	
			0.5 w/o NaF	2 w/o NaF	0.5 w/o NaF	2 w/o NaF
A	-230	Vacuum 10^{-2} mm	0.1-1.0	0.4-0.6	0.1-1.0	0.3-0.6
	-325		0.2-0.4	0.1-0.3	0.2-0.9	0.1-0.4
B	-230		0.1-0.2	0.1-0.5	0.2-0.3	0.1-0.4
	-325		0.1-0.3	0.1-0.3	0.1-0.5	0.1-0.4
C	-230		1.0-1.6	0.3-1.0	1.0-2.6	0.3-1.0
	-325		0.6-1.4	0.3-0.6	0.6-1.6	0.3-1.2
D	-230		0.8-2.0	0.4-1.6	0.7-2.2	0.4-1.8
	-325		0.6-1.0	0.4-1.3	0.8-1.2	0.3-1.2
A	-230	Argon[1] 150 mm	0.2-1.2	0.2-0.8	0.2-0.5	0.2-0.4
	-325		0.4-1.6	0.2-0.6	0.8-2.0	0.2-0.5
B	-230		0.2-0.4	0.3-0.8	0.2-0.8	0.2-0.3
	-325		0.1-0.3	0.3-0.8	0.1-1.4	0.2-1.2
C	-230		0.6-2.4	0.5-0.9	0.7-2.8	0.5-0.8
	-325		0.4-2.2	0.4-0.8	0.5-1.4	0.5-0.9
D	-230		0.7-2.0	0.4-0.9	1.2-2.8	0.6-0.8
	-325		0.4-1.0	0.8-1.2	0.6-1.6	0.6-1.4

(1) A - Double spray - 50Cr-50Ti oversprayed with 100Si
B - Double spray - 60Cr-40Ti oversprayed with 100Si
C - Co-sprayed mixture - 60Si+40(50Cr-50Ti)
D - Co-sprayed mixture - 60Si+40(60Cr-40Ti)

All weight percentages

(2) Initial furnace evacuation followed by argon backfill to 150 mm pressure
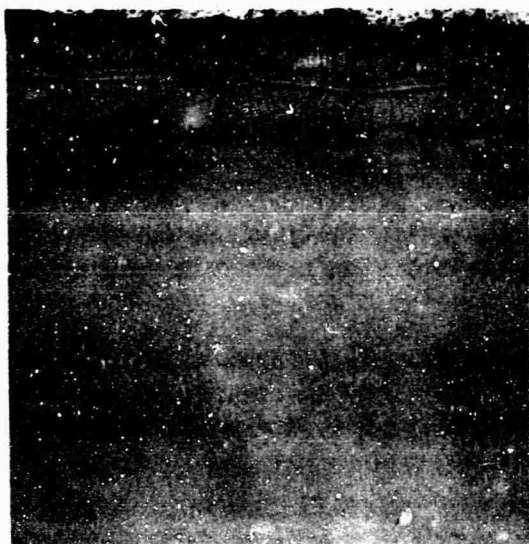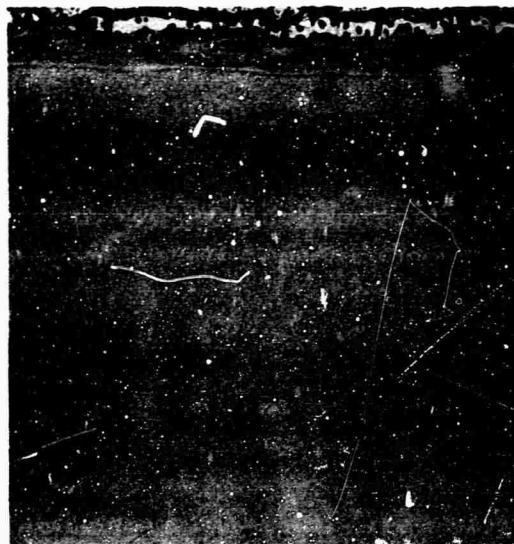
0.5 w/o NaF   2.0 w/o NaF

Vacuum
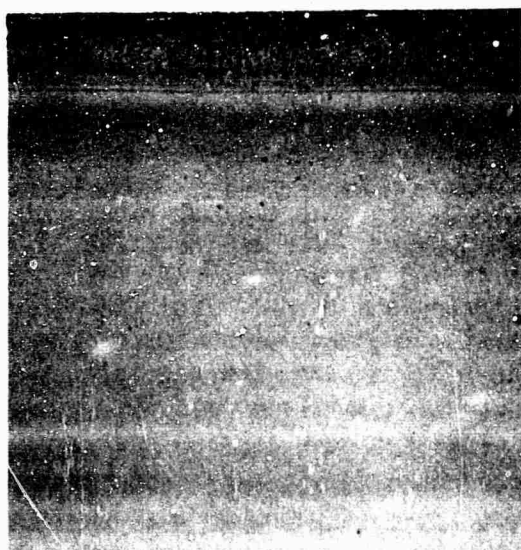
0.5 w/o NaF   Argon   2.0 w/o NaF
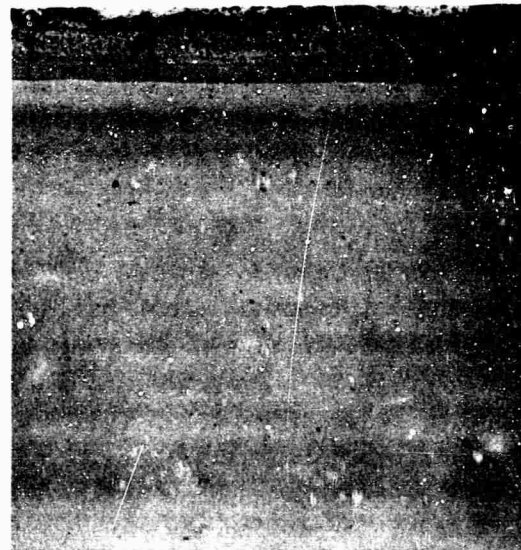
60Cr-40Ti+Si Spray Mixture

Figure 59   Cr-Ti-Si Coatings Formed on B-66 Alloys by the Spray Diffusion
Technique Using Vacuum or Argon Diffusion Environment   250X

cant alloying of the silicide with chromium or titanium occurred. It is concluded from these experiments that the two cycle Cr-Ti-Si coating can not be duplicated by a single cycle slurry-diffusion process.

6. Cr-Ti-Si COATING EVALUATION STUDIES

A series of tests were conducted to comparatively evaluate Cr-Ti-Si coatings applied on columbium base substrates by the slurry and pack processing techniques. Analyses were made of the protective reliability of these analogous coatings on D-43 and B-66 alloys, employing a sufficiently large number of replicate coupons to provide a statistically meaningful property evaluation. Comparative studies were also made of the tensile and creep properties of pack and slurry Cr-Ti-Si coated D-43 alloy. Arc plasma tests were performed on pack coated D-43, B-66 and Cb-752 alloy specimens; and cyclic oxidation tests were conducted with pack coated D-43 and B-66 coupons employing a slow rate of heating and cooling.

6.1 Reliability Analysis of the Pack Processed Cr-Ti-Si Coating

6.1.1 Specimen Preparation

Shortly before the preparation of the test coupons for the reliability analysis a technique was investigated for improving the heat-up rate of the granular Cr-Ti coating pack. The procedure involved backfilling the evacuated furnace chamber with helium gas (150 mm) to provide a heat transfer media during the heat-up cycle. The helium was introduced at approximately 500°F, after any residual water vapor had been evacuated from the warmed-up furnace, and remained in the system until the furnace temperature reached 2300°F. At this point the helium was evacuated and the coating cycle was continued at a nominal system pressure of 10^{-2} mm.

Figure 60 is a time-temperature plot comparing the pack heat-up rates in continuously evacuated and helium backfilled systems. Thermal profiles are plotted for the furnace control thermocouple, and for an internal pack thermocouple located at a mid-radius position inside the retort. The mid-radius temperature within the helium filled pack lagged the furnace control temperature by approximately 400°F at the instant the control thermocouple reached 2300°F. The corresponding temperature differential recorded in the continuously evacuated Cr-Ti pack was approximately 1500°F (Figure 2). The time required to attain temperature equilibrium between the control and internal pack thermocouples was approximately 3 hours with the helium filled retort and 5 hours with the continuous evacuation procedure. For an 8 hour coating cycle, a 50% increase in the thickness of the Cr-Ti overlay coating resulted from the improved heat transfer in the pack. Otherwise, the resulting coatings were microstructurally analogous to other pack formed Cr-Ti alloy coatings. The thickness increase was the result of the substrate materials experiencing a longer time in the temperature range in which coating formation would occur (above $\sim$ 2000°F). Based on the success of several trial coating runs using the helium backfill technique,

110
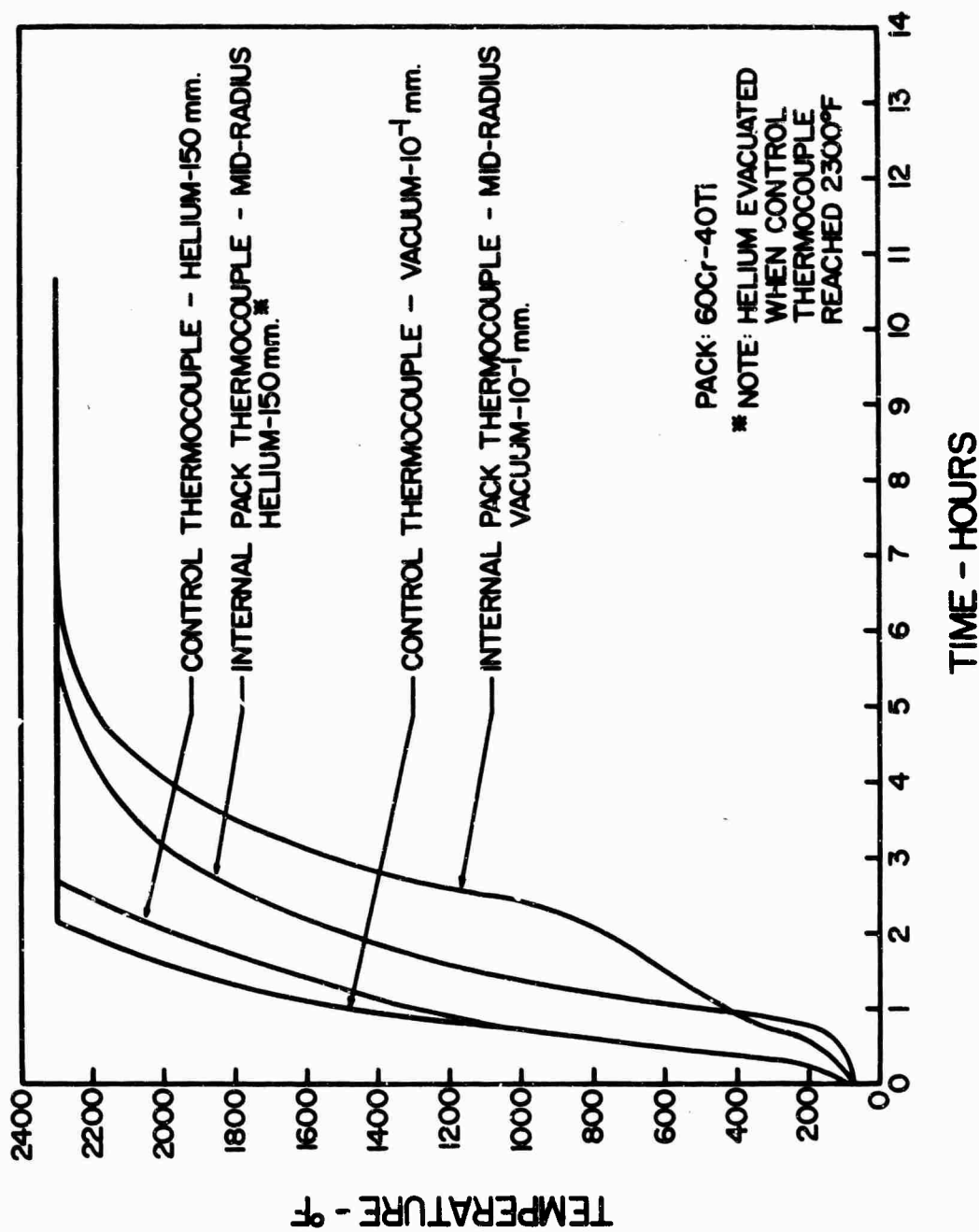
Figure 60 Temperature Profiles for 7 1/2" Diameter x 18" High Retort Comparing
Pack Heating Rate in Continuously Evacuated and Helium Backfilled
Furnace Systems

111

this procedure was selected for preparation of the reliability test coupons. Helium was not employed in the siliconizing cycle, however, since insufficient time was available to evaluate its influence on the coating formation rates and protective properties.

The pack processing parameters employed in Cr-Ti-Si coating the reliability test specimens were as follows:

Parameter	Cr-Ti Cycle	Si Cycle
Pack - w/o	60Cr-40Ti	Si
Temperature - °F	2300	2100
Time - Hours	8	6
Activator - w/o KF	0.5	1.0
System pressure - mm	10^{-2}	10^{-2}

Three identically processed specimen batches were prepared, with 70 specimens each of D-43 and B-66 alloy in each batch. All specimens were 1/2" x 1/2" sheet coupons (D-43 - 30 mil, B-66 60 mil), prepared by: (1) shearing, (2) abrasive tumbling, (3) degreasing in trichlorethylene (4) etching in an aqueous solution of 50% HF-25% H_2SO_4-10% HNO_3-15% H_2O, (5) water rinsing and (6) alcohol rinsing.

Figure 61 shows typical microstructures of the Cr-Ti and Cr-Ti-Si coatings on D-43 and B-66 alloys. Three specimens of each alloy, from each specimen batch and after each coating cycle, were metallographically prepared and observed. Batch to batch variation in coating microstructure was not marked, however, significant differences in coating thickness were observed. Table 18 lists the metallographically measured coating thicknesses representing three random samples of each alloy from each coating cycle. The Cr-Ti overlay coatings were uniform batch to batch, ranging in thickness from 0.6 to 1.0 mils, and the corresponding diffusion zones were 0.4 to 0.8 mils. More batch to batch thickness variation was observed after siliconizing, with lots No. 1 and 2 evidencing average Cr-Ti-Si coating thicknesses of 1.8 mils and lot No. 3 approximately 40% thicker at 2.5 mils.

6.1.2 Cyclic Oxidation Evaluation

Cyclic oxidation tests were conducted with the 420 test coupons at 1800(120), 2500(240), and 2700°F(60). These data are tabulated in Table 19. There were no failures observed on the 120 coated coupons tested at 1800°F after 144 hours of exposure. Thus the probability of realizing at least 144 hours protection at 1800°F, from the coatings formed in these three batches, is 100%.

All of the specimens tested at 2500°F were exposed until coating

112
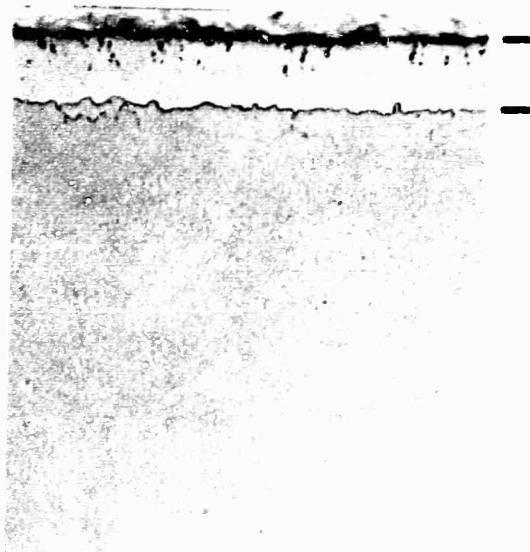
Cr-Ti   Cr-Ti-Si

B-66 Alloy

Cr-Ti   Cr-Ti-Si
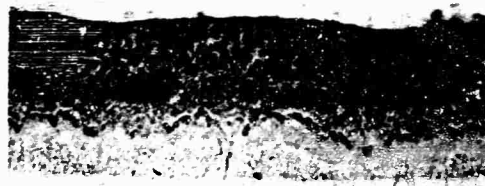
D-43 Alloy

Figure 61   Cr-Ti and Cr-Ti-Si Pack Coatings on B-66 and D-43 Alloys -
            Reliability Study
                                                              500X

113

TABLE 18

Metallographic Results of Pack Processed Cr-Ti and Cr-Ti-Si Coatings on D-43 and B-66 Alloys - Reliability Study[1]

Substrate Alloy	Batch No.	Sample No.	Cr-Ti Coating Mils[2] Overlay	Cr-Ti Coating Mils[2] Diffusion Zone	Cr-Ti-Si Coating Mils[2] Overlay	Cr-Ti-Si Coating Mils[2] Diffusion Zone
D-43	1	1	0.6-0.8	0.3-0.4	2.0	0.4
		2	0.6-0.8	0.4	1.8	0.4
		3	0.7-0.8	0.4	1.8	0.4
	2	1	0.8	0.4	2.0-2.2	0.4
		2	0.8	0.4	2.0	0.4
		3	0.6-0.8	0.4-0.6	1.8	0.4
	3	1	0.6-0.8	0.4-0.6	2.4-2.6	0.4
		2	0.8-1.0	0.4-0.6	2.0-2.4	0.4
		3	0.6-0.8	0.4-0.6	2.4	0.4
B-66	1	1	0.7-0.8	0.6	1.6-1.8	0.6
		2	0.6-0.8	0.6-0.8	1.8-2.4	0.4
		3	0.6-0.8	0.4-0.6	1.7-2.0	0.6-0.8
	2	1	0.6	0.6	1.6-1.8	0.4
		2	0.6	0.6	1.8-2.0	0.4
		3	0.8	0.4	1.4-1.6	0.6-0.8
	3	1	0.7-0.8	0.6-0.8	2.3-2.9	0.4
		2	0.6-0.8	0.4-0.6	2.2	0.4
		3	0.6-0.8	0.4-0.6	2.9-3.0	0.4

(1) Processing parameters - page 112

(2) Metallographic measurements

overlay
diffusion zone
substrate

114
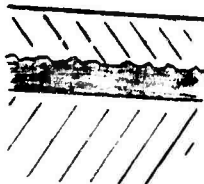
TABLE 19

Cyclic Oxidation Test Results of Pack Processed Cr-Ti-Si Coatings on
D-43 and B-66 Alloys -
Reliability Study

Substrate	Test Temperature - °F	Protective Life - Hours(a)		
		Batch No. 1	Batch No. 2	Batch No. 3
D-43	1800	>144(20)(b)	>144(20)	>144(20)
	2500	76,97,76,104,80,96,76,101 96,104,104,96,120,168,192,72 120,168,72,192,128,98,120 120,120,96,96,104,125,149,96 120,144,128,120,128,103,103	120,104,102,120,152,72,151,103 104,104,104,73,74,120,160,72 144,72,96,127,144,96,120,120 120,96,120,127,120,74,74,96 96,74,120,96,101,96,128,120	120,76,96,125,96,96,144,78,96 103,102,72,101,160,49,160,49 56,120,1 ,120,120,72,120,144 78,106,21,120,72,96,120,121 96,130,96,130,96,96,77
	2700	22,29,25,29,70,29,21,21,21 13	45,37,36,26,50,33,37,43,35,33	96,12,83,19,96,87,96,21,68
B-66	1800	>144(20)		>144(20)
	2500	96,96,151,96,78,98,202,78,96 120,72,102,128,120,168,192 121,168,96,104,104,15 ,120 120,101,191,104,128,120,120 120,120,120,120,103,101,120 100,104,174	104,269,125,216,96,144,151,211 125,73,120,168,144,192,152,216 216,120,138,157,140,141,157,157 158,165,157,138,141,191,157,157 158,157,177,182,158,157,191,158	173,104,168,174,144,101,98,192,120 78,125,106,144,168,192,159,143,158 158,135,158,140,142,39,140,141,156 135,139,143,145,144,192,119,170,140 142,158,135,158
	2700	29,44,62,44,45,58,26,43,41,3	18,96,19,19,33,30,27,27,53,31	27,49,26,27,30,56,28,23,91,40

(a) Oxidation test procedure - See Table 3

(b) Denotes number of replicate samples

115

failure. Plotting these protective life data as frequency polygons indicated that the data were non-Gaussian in distribution, and therefore some error is introduced in treating these data by conventional statistical methods, such as the calculation of sample mean and standard deviation values. However, in order to compare these data with the protective reliability data obtained in a previous program (AF 33(657)-7396), the standard deviation calculations were made. The substrates were considered individually in this treatment, and the specimen batches were combined into one sample lot. For less than an infinite sample population:

$$\mu \text{ (true mean)} \sim \bar{X} \text{ (sample mean)}$$

$$\sigma \text{ (true deviation)} \sim S \text{ (sample deviation)}$$

$$\bar{X} = \frac{1}{N} \sum_{i=1}^{N} x_i = \frac{1}{N} (X_1 + X_2 + X_3 + \dots\dots X_N)$$

$$S = \sqrt{\frac{1}{N-1} \left[\sum_{i=1}^{N} x_i^2 - \frac{(\sum x_i)^2}{N} \right]}$$

where: x_i = any test value

N = total number of samples

These calculations for the 2500°F oxidation test data are listed in Table 20. A comparison of these data with similar data from a previous program (Table 29 ASD TDR-62-934, Part II)[2], indicates approximately a 60% improvement in the 2500°F mean protective life of the Cr-Ti-Si coating (middle retort position), attributed to the utilization of improved materials and processing parameters in this program.

Protective probability levels were also reported for the previous reliability data, and a comparison of these values for the two programs is also appropriate. In calculating the probabilities it must be assumed that $\bar{X}$ and S are significant quantities for these data, although it is recognized that error does exist owing to the skewed distribution of the failure data. These calculations were made in the following manner:

116

TABLE 20

Statistical Data for Protective Properties of Pack Processed Cr-Ti-Si Coatings on D-43 and B-66 Alloys at $2500°F$ [1]

Batch No.	Substrate						
	D-43				B-66		
	$\bar{X}$	S	N		$\bar{X}$	S	N
1	116	31	40		115	25	40
2	108	24	40		158	36	40
3	104	27	40		144	25	40

(1) $\bar{X}$ - Mean Protective Life

S - Standard Deviation

N - Number of Replicate Samples

117
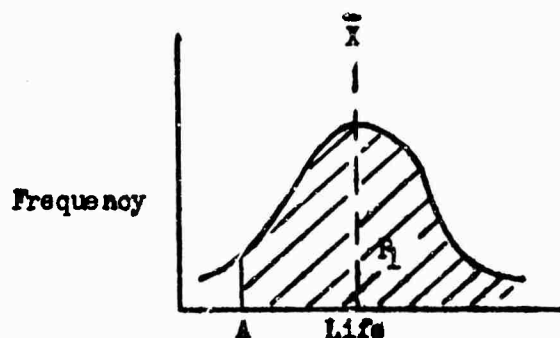
1. The probability of a specimen attaining a minimum life A is given by the area P_1 under the frequency distribution curve.

2. For an assumed value P_1, the life A is determined from

$$\bar{X} - K \cdot S = A \quad \text{or} \quad \bar{X} + K \cdot S = A \text{ if A exceeds } \bar{X}$$

   where the value of K corresponding to P_1 is obtained from a table of "Percentiles of Normal Distribution".

3. The true mean (μ) for an infinite data population will lie within the confidence interval for the sample mean, which is established from the relation

$$\bar{X} \pm K_c \left(\frac{S}{\sqrt{N}} \right)$$

   where K_c corresponds to the percentile value of the desired confidence level (99 percent), and is obtained from a standard Student's t Distribution Table.

4. The confidence interval on $\bar{X}$ is then transposed to a confidence interval on the desired probability level, using the following expressions

$$K_a = \frac{\bar{X} + K_c \left(\frac{S}{\sqrt{N}} \right) - A}{S}$$

$$K_b = \frac{\bar{X} - K_c \left(\frac{S}{\sqrt{N}} \right) - A}{S}$$

   where K_a and K_b are the upper and lower limits on the probability P_1 for a protective life A. Table 21 lists the probability values for the 2500° F oxidation data generated in this program.

118

TABLE 21

Cr-Ti-Si Coating Protective Reliability at 2500°F

99% Confidence Level

D-43 Alloy		B-66 Alloy	
Probability	Life - Hours	Probability	Life - Hours
97.5 + 1.8%	59	97.5 ± 2.0%	82
95 ± 1.7%	64	95 ± 1.7%	91
90 ± 1.3%	74	90 ± 1.3%	102
75 ± 0.7%	91	75 ± 0.6%	120

For D-43 alloy the 97.5% probable protective life of the Cr-Ti-Si coating is 59 hours, at a confidence level of 99%. The corresponding life for the coating on B-66 is approximately 40% higher at 82 hours. Comparing these probability levels with those obtained for these systems in the previous program (Table 30 - ASD TDR-62-934 Pt II)[2], a 3-4 fold improvement in the 97.5% probable 2500°F protective life of the Cr-Ti-Si coating was realized in the current program.

These protective life data are also plotted to the Weibull distribution as shown in Figures 62 and 63. The Weibull distribution[10] is a cumulative frequency function expressed by

$$F(t) = 1 - \exp \left(\frac{\alpha - t}{\theta}\right)^{\beta}$$

where: $F(t)$ = cumulative failures expressed as a fraction of the sample lot

α = threshold parameter (normally zero)

t = time

θ = failure time corresponding to 63.2 percent of the sample population

β = slope or shape parameter (> 0)

A single failure mode is delineated by the Weibull distributions, representing a wearout type of coating failure mechanism. Very little batch to batch variation is exhibited by these data, and the relatively steep slopes of the function represent a uniform protective behavior within the sample lots. The superior performance of the Cr-Ti-Si coating on B-66 alloy, as opposed to D-43 alloy, is clearly evident from the graphs.

The 2700°F oxidation test data were also tabulated in Table 19. Considering the small sample lots and the skewed character of the frequency distributions, no effort was made to apply standard deviation methods to these data. The data are plotted to the Weibull distribution, as shown in Figures 64 and 65. Comparing the 50% cumulative failure times from the Weibull graphs with the mean 2700°F protective times obtained in the previous program (Table 29 - ASD TDR-62-934 - Pt II)[2], 5 and 8 fold improvements in the 2700°F protective lives of the Cr-Ti-Si were realized on D-43 and B-66 alloys, respectively, in the current program.

More batch to batch property variation is exhibited by the 2700°F test data than was evidenced by exposing the coatings at 2500°F. For D-43 alloy, batch No. 3 shows the shallowest slope for the Weibull distribution; and on B-66 alloy the batch No. 3 coatings appear to delineate a bimodal failure mechanism. In both cases, the characteristics of the distributions are probably attributed to variations in coating thickness, as suggested

120
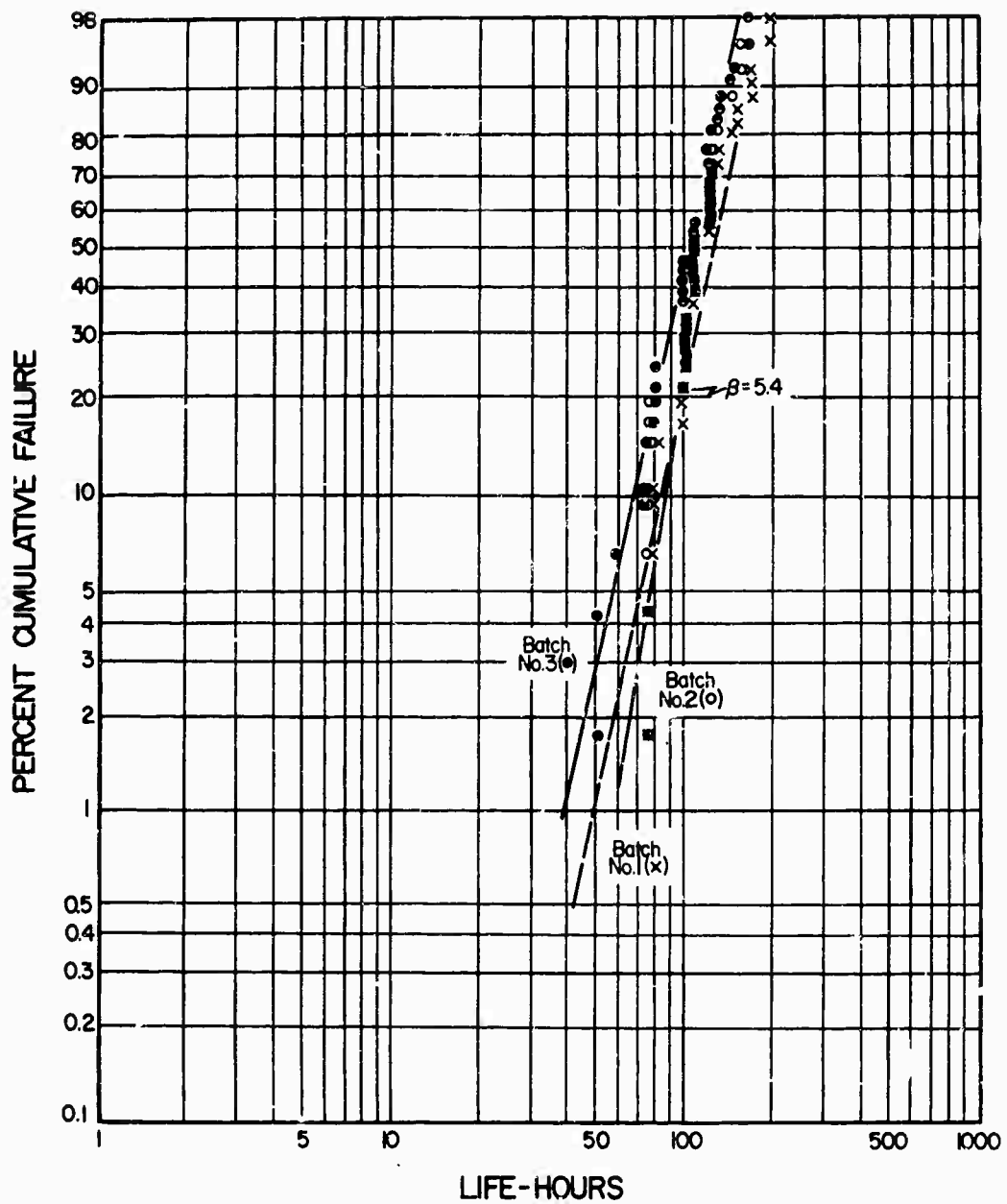
Figure 62 Weibull Plot of 2500° F Cyclic Oxidation Test Results of Pack
Processed Cr-Ti-Si Coating on D-43 Alloy

121
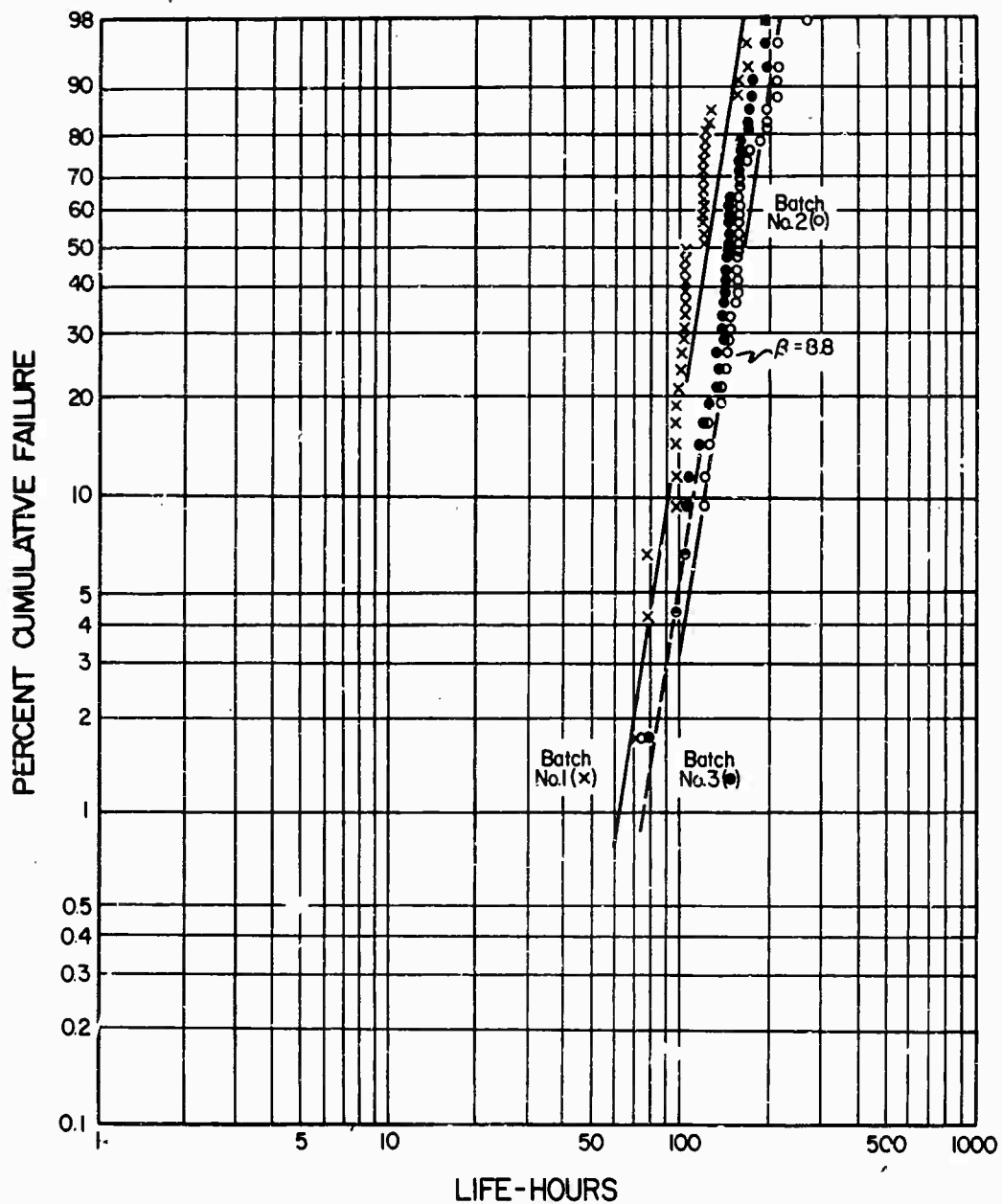
Figure 63 Weibull Plot of 2500°F Cyclic Oxidation Test Results of Pack
Processed Cr-Ti-Si Coating on B-66 Alloy

122
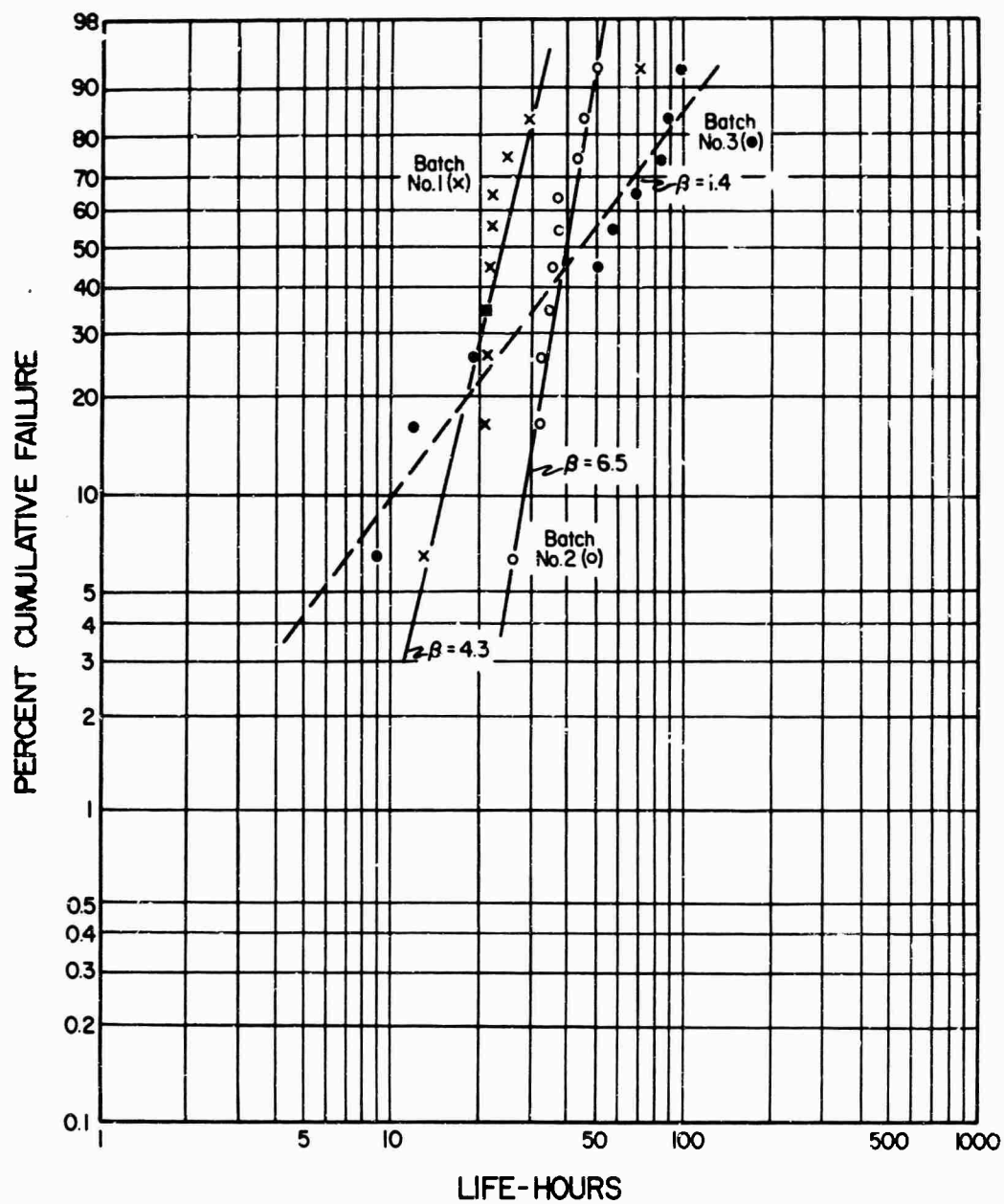
Figure 64 Weibull Plot of 2700° F Cyclic Oxidation Test Results of Pack
Processed Cr-Ti-Si Coating on D-43 Alloy
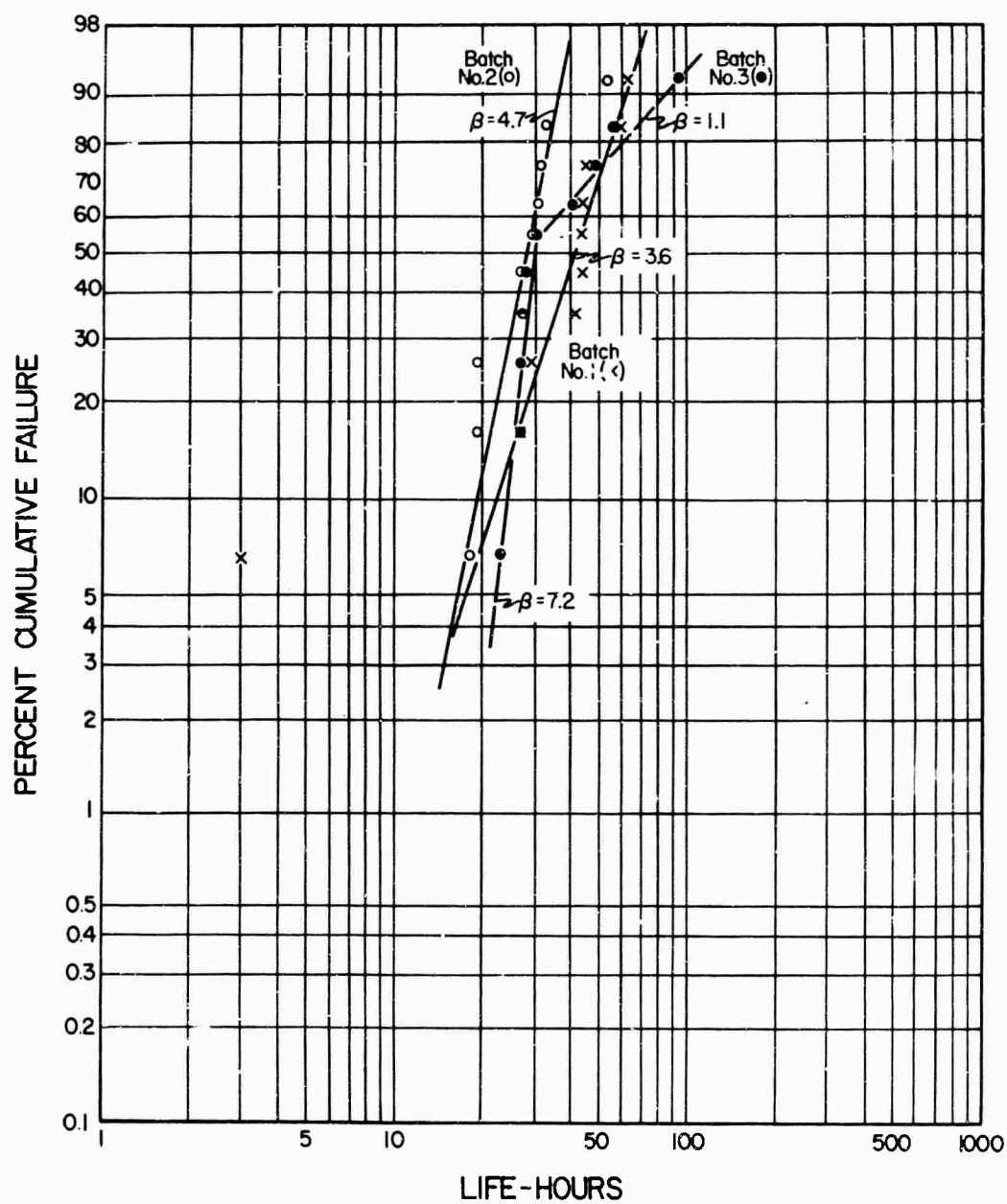
Figure 65   Weibull Plot of 2700° F Cyclic Oxidation Test Results of Pack
Processed Cr-Ti-Si Coating on B-66 Alloy

124

by the metallographic data reported in Table 18.

In comparing the current reliability study with that conducted under Contract AF 33(657)-7396, it is evident that the Cr-Ti-Si coating evaluated in the previous program represented protective properties which were inferior to the current capabilities of the Cr-Ti-Si system. The processing parameters and pack materials utilized in the previous program produced Cr-Ti-Si coatings which evidenced insufficient chromium and titanium in the disilicide and in the substrate diffusion zone. The thicker Cr-Ti coatings produced in this program resulted in Cr-Ti-Si coating chemistries which were substantially richer in chromium and titanium, hence the improved protective performance. Although the reliability study conducted in this program was far less extensive, the data generated are a more representative evaluation of the protective capabilities of the vacuum pack Cr-Ti-Si coating on columbium base materials.

6.2 Oxidation Evaluation of Spray Processed Cr-Ti-Si Coatings

6.2.1 Specimen Preparation

The spray processed Cr-Ti-Si coatings were formed on the columbium alloy coupons according to the procedures discussed previously in Section 5. Two specimen batches consisting of 80 specimens each of D-43 and B-66 alloys were coated for oxidation testing. The processing parameters were as follows:

	Cr-Ti Cycle	Silicon Cycle
Slurry-metal (w/o)	90 (50Cr-50Ti) + 10Ti	100 Si
Temperature	2300°F	2000°F
Time	8 Hours	3 Hours
System Pressure (argon)	150 mm	150 mm
Bisque Thickness	>10 mils	>10 mils

The sprayed bisques were diffusion treated in the pilot-scale induction heated coating furnace employing a getter sealed retort 5" diameter x 10" high. Insufficient space was available in the experimental size furnace for coating the larger groups of test coupons. Figures 66 and 67 are photomicrographs of representative coatings from these runs.

In both batches, the coating vapor phase in the Cr-Ti cycle was apparently too rich in titanium, which resulted in excessive coating element diffusion and the intermittent absence of a Cr-Ti alloy overlay on the substrate surface. The preliminary diffusion runs in this furnace involved the application of coatings on only 8 to 10 specimens per lot, as opposed to 80 specimens per group in the reliability analysis. The processing parameters established for the 8-10 coupon lots were not adequate for the larger specimen batches, apparently owing to the greater quantity of activator/furnace volume provided in the larger specimen groups.

125

Cr-Ti   Cr-Ti-Si
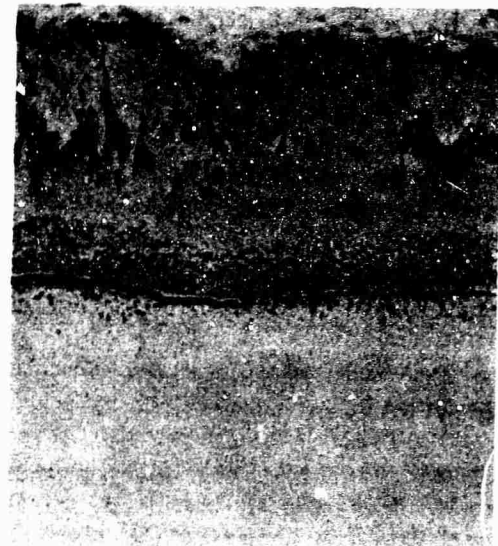
B-66 Alloy

Cr-Ti   Cr-Ti-Si

D-43 Alloy

Figure 66   Cr-Ti and Cr-Ti-Si Slurry Coatings on B-66 and D-43 Alloys - Reliability Study - Batch No. 1   500X

126

Cr-Ti   Cr-Ti-Si
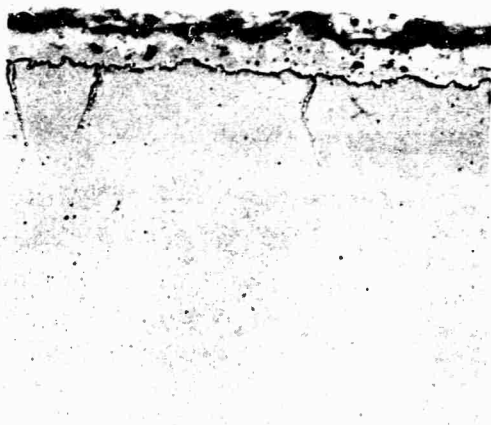
B-66 Alloy

Cr-Ti   Cr-Ti-Si

D-43 Alloy

Figure 67 Cr-Ti and Cr-Ti-Si Slurry Coatings on B-66 and D-43 Alloys -
Reliability Study - Batch No. 2   500X

127

An excess of activator ar a longer residence time of the activator in the presence of the coating elements favors a higher concentration of the titanium coating species in the vapor phase.

A second deficiency in these spray process coatings is associated with the siliconizing cycle. Oxidation of the Cr-Ti coating apparently occurred during the siliconizing cycle, resulting in oxide precipitation, and in some areas cracking or separation at the silicide-substrate interface. Preliminary siliconizing runs were not made in this furnace system prior to preparation of the reliability test specimens. Apparently considerably more residual oxygen was present in this furnace than in the smaller experimental furnace, and this oxygen was gettered principally by the titanium constituent in the Cr-Ti alloy coating. Cracking at the coating-substrate interface was quite pronounced with the batch No. 1 D-43 alloy coupons.

Metallographic measurements were utilized to determine the coating thicknesses on random samples from each specimen batch. These data are presented in Table 22. Continuous Laves phase overlays were observed on all D-43 coupons, although ranging in thickness from 0.2-0.6 mils. Cr-Ti alloy overlays on B-66 alloy ranged from nil to 0.6 mils. Siliconizing produced 2.2-3.2 mils Cr-Ti-Si coatings on these specimens, which is comparable in thickness to the pack processed coatings prepared for the reliability analysis.

6.2.2 Cyclic Oxidation Evaluation

Cyclic oxidation evaluation tests were conducted with the 160 coupons at 1800(40), 2500(88), and 2700°F(32). These data are presented in Table 23. Ten specimens of each alloy, from each batch, were tested at 1800°F. One D-43 coupon and two B-66 coupons from batch No. 1 failed prior to the test termination time of 144 hours. These failures were defect orientated, and were undoubtedly associated with the observed interfacial cracking or the localized deficiencies in the original Cr-Ti coating.

Twenty-two specimens of each alloy, from each sample lot, were oxidation tested at 2500°F. These data are plotted to the Weibull density function, as shown in Figures 68 and 69. A pronounced batch to batch variation existed between the two sample lots, with batch No. 1 evidencing a bimodal failure distribution and batch No. 2 a single mode. The short-time failure mode in batch No. 1 is a defect mechanism, whereas the longer time failure mode is a wearout type phenomenon. The 50% cumulative failure time of the batch No. 2 coatings is observed to be comparable to the analogous value for the pack processed Cr-Ti-Si coatings, as shown by a comparison of the Weibull plots.

Figures 70 and 71 are Weibull plots of the 2700°F oxidation test data for the spray processed Cr-Ti-Si coatings. Eight specimens of each alloy, from each specimen batch, were tested at this temperature. Considerably less batch to batch variation is exhibited by 2700°F test data, although

128

TABLE 22

Metallographic Results of Spray Processed Cr-Ti and Cr-Ti-Si Coatings
on D-43 and B-66 Alloys[1] - Reliability Analysis

Substrate Alloy	Batch No.	Cr-Ti Coating Mils[2]		Cr-Ti-Si Coating Mils[2]	
		Overlay	Diffusion Zone	Overlay	Diffusion Zone
D-43	1	0.4-0.6	1.0	2.2-3.2	0.4-0.6
	2	0.2-0.4	1.0-1.4	2.2-2.4	0.8-1.0
B-66	1	0-0.6	1.2-1.4	2.4-2.6	0.8-1.0
	2	0-0.6	1.0-1.4	2.2-2.4	0.8-1.0

(1) Processing conditions - page 125

(2) Metallographic measurements

overlay
diffusion zone
substrate

129
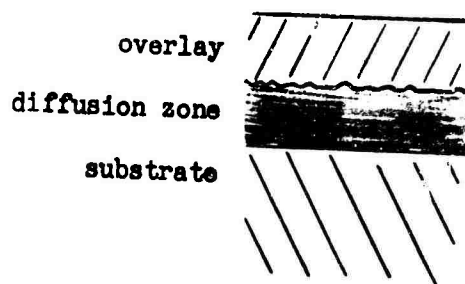
TABLE 23

Cyclic Oxidation Test Results of Spray Processed Cr-Ti-Si Coating
on D-43 and B-66 Alloys - Reliability Analysis

Substrate	Test Temperature – °F	Protective Life – Hours(a)	
		Batch No. 1	Batch No. 2
D-43	1800	>144(9)(b) 24(1)	>144(10)
	2500	48,24,7,7, 5,72,7,5,7,8,8 72,7,7,7 , 3,5,7,8,8	72,97,125,120,120,152,72,120 120,120,120,125,97,72,144,125, 125,144,56,120,120
	2700	40,59,49,5,,50,26,46,22	68,58,35,64,55,28,54,59
B-66	1800	>144(8) 24(1) 4(1)	>144(10)
	2500	125,144,8,2,2,2,172,2,224 24,24,24,101,24,264,120,200 192,224,200,144,8	96,127,170,170,152,174,101,175 120,79,24,96,168,56,146,151,192 151,150,146,148,200
	2700	2,3,62,48,59,14,47,51	22,3,8,14,3,22,14,3

(a) Oxidation test procedure - See Table 3

(b) Denotes number of replicate samples

130
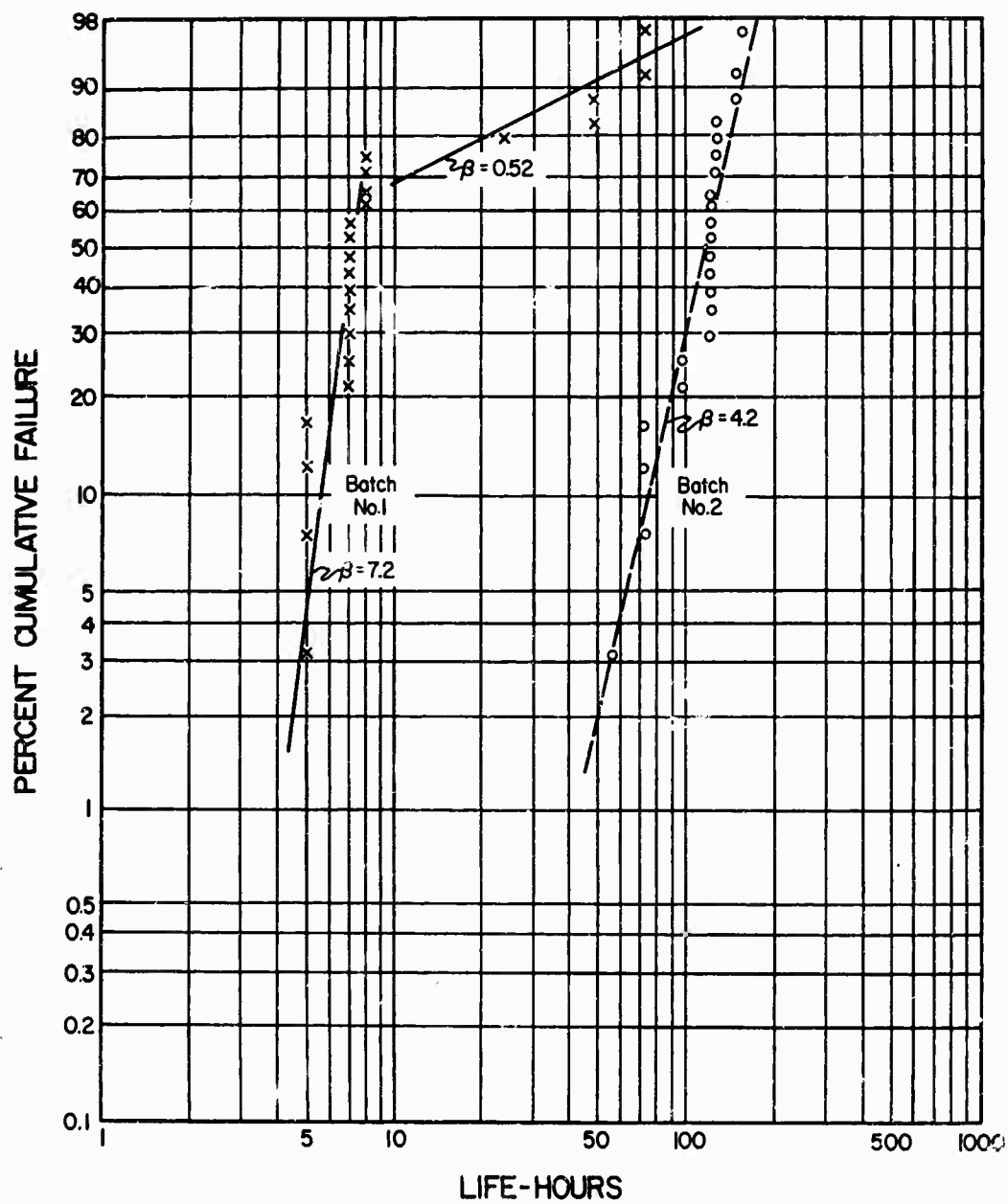
Figure 68   Weibull Plot of 2500°F Cyclic Oxidation Test Results of Spray
Processed Cr-Ti-Si Coating on D-43 Alloy

131
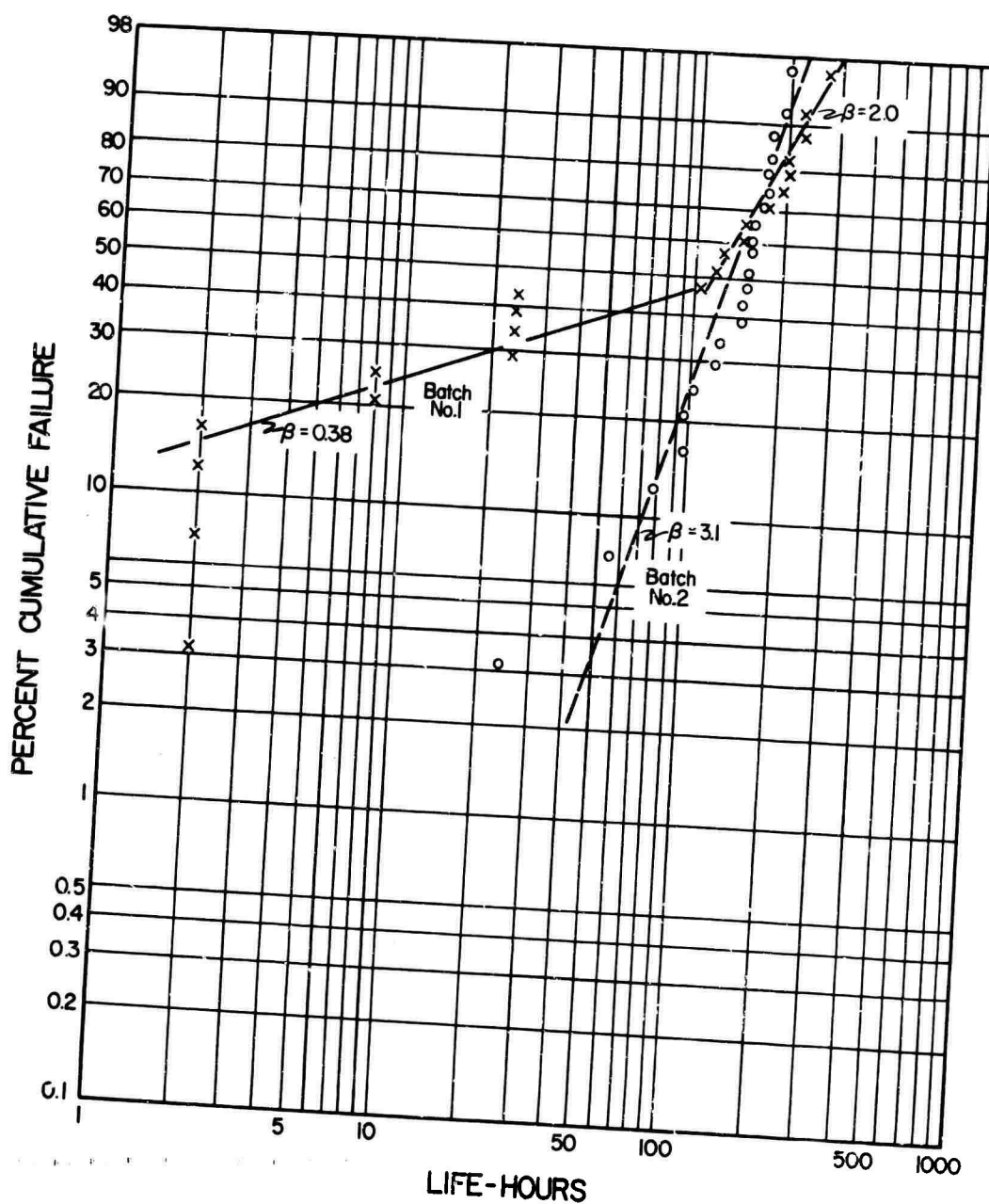
Figure 69 Weibull Plot of 2700°F Cyclic Oxidation Test Results of Spray Processed Cr-Ti-Si Coating on B-66 Alloy

132
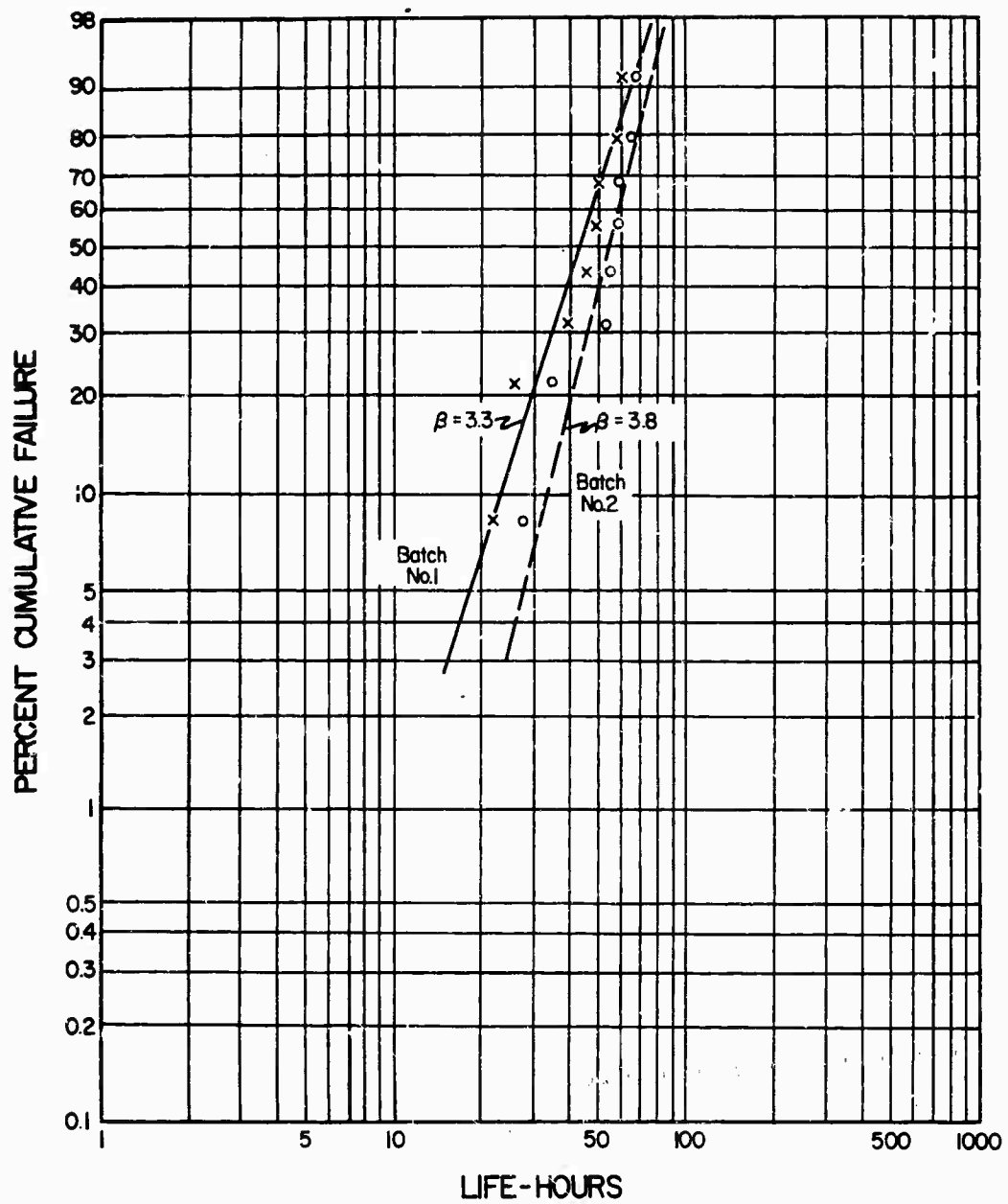
Figure 70 Weibull Plot of 2700°F Cyclic Oxidation Test Results of Spray
Processed Cr-Ti-Si Coating on D-43 Alloy

133
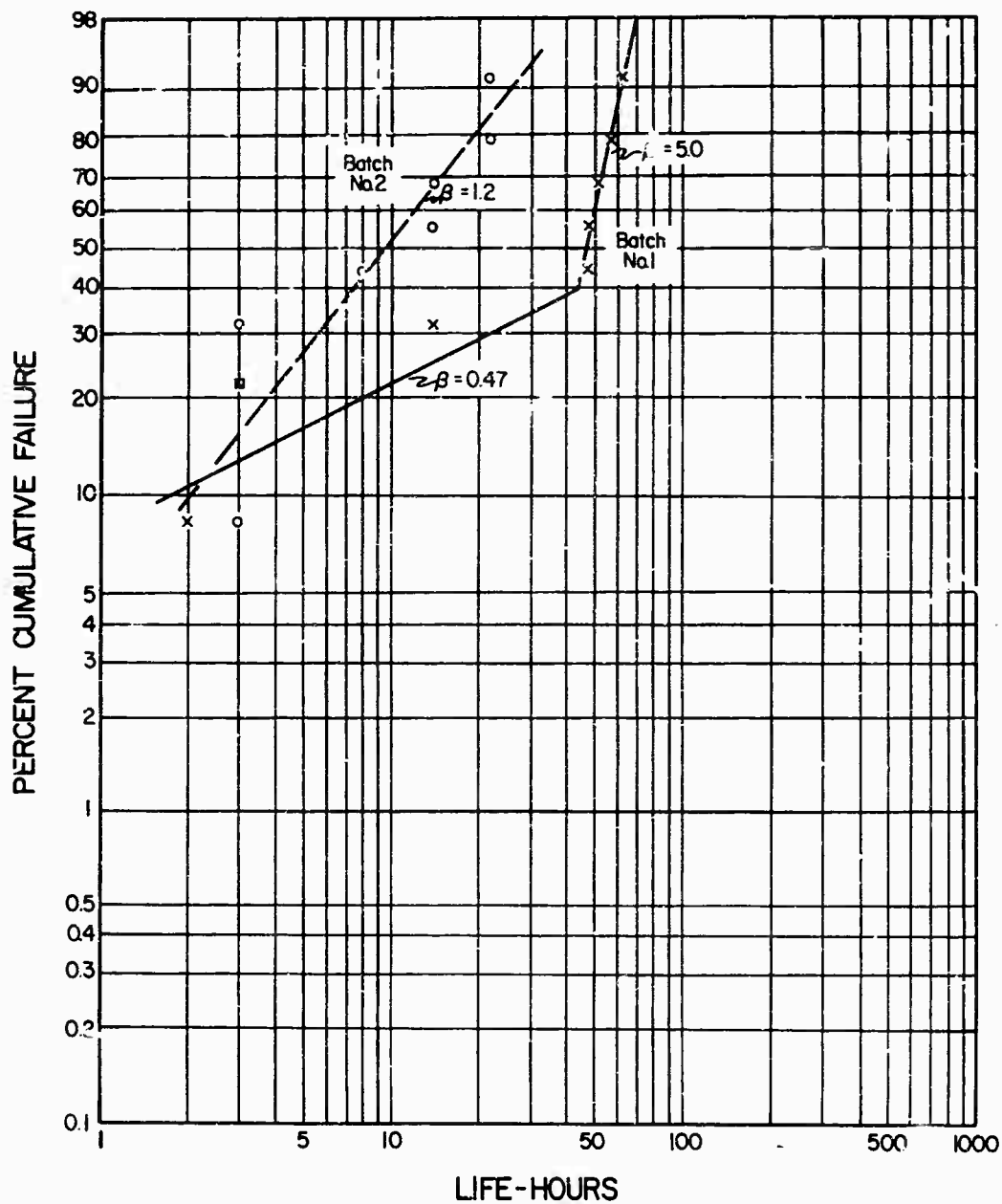
Figure 71   Weibull Plot of 2700°F Cyclic Oxidation Test Results of Spray
Processed Cr-Ti-Si Coating on B-66 Alloy

134

batch No. 1 still evidenced a bimodal failure distribution. Note that the batch No. 1 coatings were superior on D-43 alloy and the batch No. 2 coatings on B-66 alloys. Again comparing the better specimen batches, the 50% cumulative failure times for the spray and pack processed Cr-Ti-Si coatings were comparable on both alloys.

The oxidation evaluation of the spray processed Cr-Ti-Si coatings was successful in demonstrating both the attractive potential and the current lack of reliability of the spray processed Cr-Ti-Si coating. It appears quite plausible that the spray-diffusion Cr-Ti-Si coating process can be advanced to a technological level comparable to that of the vacuum pack coating process. Additional development work is recommended in this area.

6.3 Cyclic Oxidation - Pack Cr-Ti-Si Coatings - Profiled Thermal Cycle

The cyclic oxidation screening test generally employed in evaluating oxidation protective coatings involves inserting the coupons directly into a heated furnace, followed by periodically air cooling the specimens for visual inspection. In this case the heating and cooling rates are relatively rapid, and the time during which the coated material experiences low and intermediate temperatures is quite small. Oxidation studies with the Cr-Ti-Si coating and other silicide coatings at Solar[4] and TRW have indicated that a slow rate of heating and cooling is frequently a more severe test criteria than the conventional thermal cycling. The reason for this behavior is apparently associated with a low temperature failure phenomenon which operates over only a very narrow temperature range for a specific coating composition. This temperature region is passed through very rapidly in conventional thermal cycling, leaving insufficient time for this type oxidation.

The profiled heating and cooling cycle employed in this brief study was accomplished by exposing coated specimens in a box type furnace during the normal furnace heating and cooling cycle. The specimens were held at the peak temperature of 2500°F for 1/2 hour prior to cooling. The cycle (approximately 7 hours) is shown in Figure 72, and involved heating and cooling in the temperature range from 800 to 2500°F.

Two groups of Cr-Ti-Si coated D-43 and B-66 alloy coupons (20 each alloy) were evaluated in this study. The coating parameters were as follows:

Pack w/o	Activator w/o	Temp. °F	Time-Hours	Pressure-mm
		Group A		
60Cr-40Ti	0.5 KF	2300	8	10^{-2}
Si	1.0 KF	2100	6	10^{-2}

135
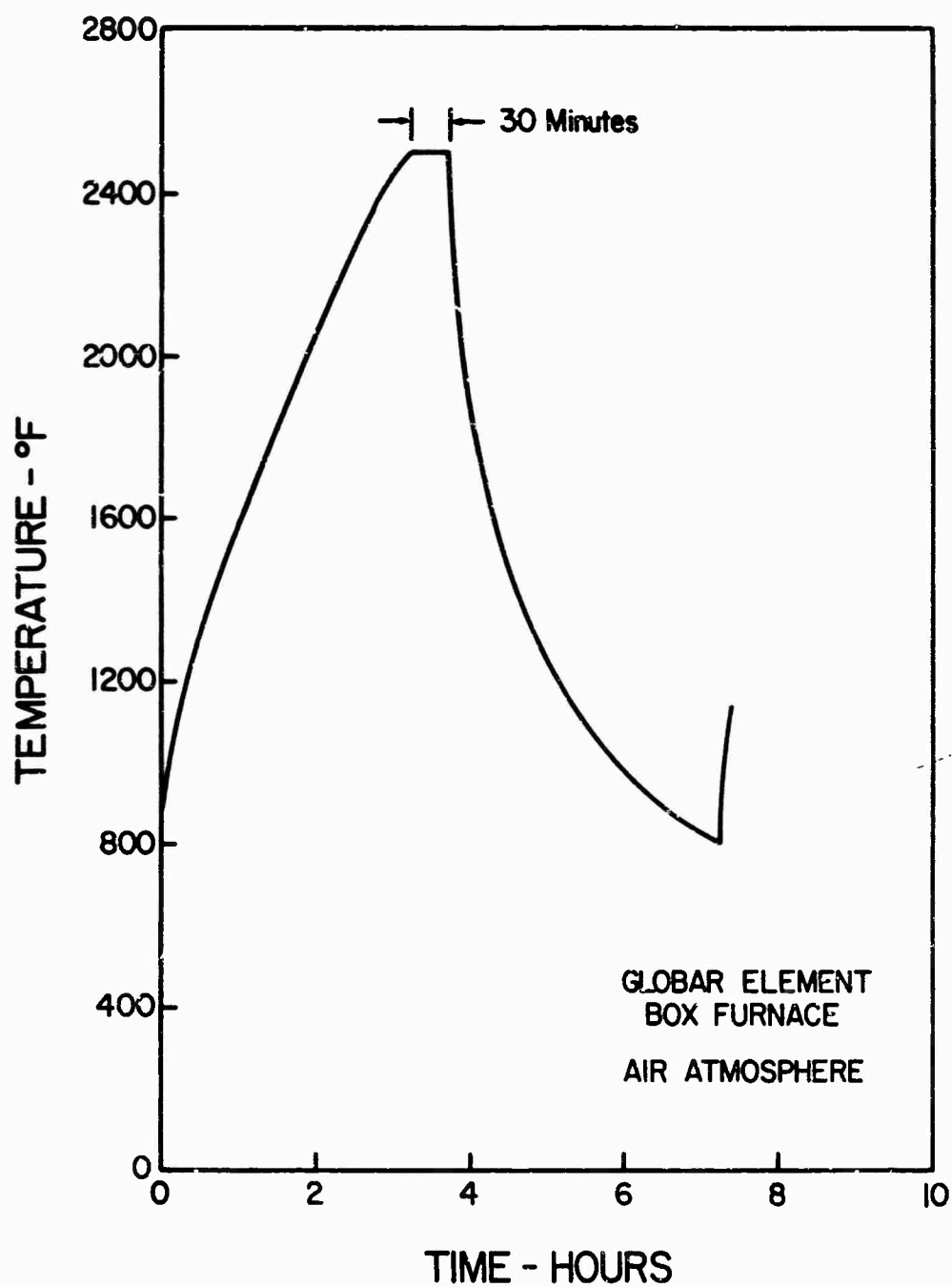
Figure 72 Thermal Profile of Slow Heat - Slow Cool Oxidation Test Cycle

136

Pack w/o	Activator w/o	Temp.°F	Time-Hours	Pressure-mm
		Group B		
60Cr-40Ti	0.5 KF	2340	12	1.5
Si	1.0 KF	2100	6	10^{-2}

Group A represents the parameters used in preparing the reliability test coupons (Section 6.1), and Group B the parameters utilized in preparing the arc plasma test specimens (Section 6.5). Photomicrographs representative of these coatings on D-43 alloy are shown in Figure 73. Considerably more chromium and titanium diffusion into the columbium substrate, and a slightly thicker Cr-Ti overlay, resulted from the higher temperature - longer time processing parameters (Group B).

Prior to subjecting these coupons to the profiled thermal cycle, half of the specimens (10 each alloy) were given a 2 hour preoxidation in air at 2500°F. The purpose of this pretreatment was to form a protective oxide on the coating surface prior to any sustained exposure at a lower temperature. A maximum of twelve thermal cycles were performed with the forty specimens, and the results of this study are presented in Table 24.

The majority of the D-43 specimens (15 of 20) failed in less than 12 thermal cycles, whereas only 1 of 20 B-66 coupons evidenced coating failure after 12 cycles. In all cases failure constituted a localized growth(s) of oxide through the coating, and generally only one or two spots were evident. The Group B D-43 coupons were less susceptible to failure than were the Group A specimens, and this was anticipated based on the more thorough alloying of the substrate surface with chromium and titanium by the Process B parameters. The lower susceptibility of the coated B-66 substrate to failure is also consistent with other oxidation data, which indicate a relatively greater protective reliability of the Cr-Ti-Si coating on the B-66 alloy. Pre-oxidation at 2500°F appears to have enhanced the onset of the low temperature failure mechanism.

A comparison of these data with conventional cyclic oxidation results involving both high (2500°F) and intermediate (1800-2000°F) temperature exposure conditions does suggest the presence of a low temperature failure mechanism in the Cr-Ti-Si system. Susceptibility to low temperature failure is not an uncommon property of basic silicide systems on refractory metals, and in these systems the phenomenon is generally operative over a wide range of temperatures and exposure conditions. With the Cr-Ti-Si system the susceptibility to low temperature failure is quite compositionally dependent, and the time-temperature conditions for this type of oxidation are apparently very critical. A far more extensive effort in this area would be required to understand and characterize this type of low temperature failure phenomena in the Cr-Ti-Si system.

Cr-Ti   Cr-Ti-Si

Group A
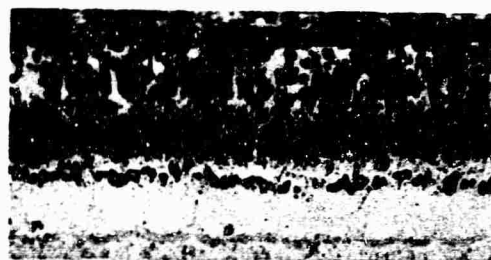
Cr-Ti   Cr-Ti-Si

Group B

Figure 73   Cr-Ti and Cr-Ti-Si Coatings on D-43 Alloy - Specimens for Profiled
Oxidation Thermal Cycle
500X

138

TABLE 24

Protective Properties of the Cr-Ti-Si Coating on D-43 and B-66 Alloys for a Thermal Profiled Oxidation Cycle

Coating Group	Substrate	Cycles to Failure[1]	
		As Coated	Preoxidized 2500°F[2]
A	D-43	8,9,9,9,10	8,9,9,9,9
	B-66	>12(5)[3]	>12(5)
B	D-43	9, >12(4)	9,9,11,11, >12
	B-66	8, >12(4)	>12(5)

(1) Thermal cycle - See Figure 72

(2) Preoxidation - 2 hours - 2500°F - air cool

(3) Replicate coupons

6.4 Mechanical Property Comparison of Pack and Slurry Coated D-43 Alloy

A comparison was made of the tensile and creep properties of pack and slurry Cr-Ti-Si coated D-43 alloy sheet. The pack and slurry coatings were applied on the test specimens in conjunction with the preparation of coupons for the reliability analyses. The process parameters were outlined previously in Sections 6.1 and 6.2. Figure 74 shows the specimen configurations utilized in these tests.

6.4.1 Tensile Properties

Tensile tests were performed on coated and uncoated D-43 alloy sheet at room temperature, 2000 and 2500°F. All tests were conducted in an Instron tensile machine, in accordance with the test procedures recommended by the Materials Advisory Board (MAB-201-M)[11]. For room temperature tests a crosshead travel of 0.005 in/min. was employed to at least 0.6% offset, and then increased to 0.050 in/min. thereafter until fracture. At 2000 and 2500°F the rate of crosshead travel was maintained at 0.050 in/min. from zero strain to fracture. The elevated temperature tests on uncoated and Cr-Ti coated D-43 sheet were conducted in a resistance heated (tantalum element) Brew vacuum furnace. Quartz lamp radiant heating was employed in the 2000 and 2500°F air tests of Cr-Ti-Si coated D-43 sheet. The specimen temperature was monitored with a Pt-Pt+10% Rh thermocouple. At room temperature a gage extensometer was used to record load-strain curves. However, at the elevated temperatures the heating equipment precluded the use of an extensometer, thus load-extension curves based on crosshead travel were used for the load determinations. Original substrate dimensions were utilized for all stress calculations.

Concurrently with the comparison of the properties of pack and slurry coated material, an evaluation was also made of the influence of the coating and coating process on the absolute properties of the D-43 sheet. This was accomplished by testing material in five conditions: (1) uncoated, (2) Cr-Ti coated, (3) Cr-Ti coating removed, (4) Cr-Ti-Si coated and (5) Cr-Ti-Si coating removed. The coatings were removed by alternately abrasive blasting and acid etching until the coating and coating affected substrate was completely removed. The tensile properties from this series of tests are presented in Tables 25 and 26.

A comparison of the properties of slurry and pack coated D-43 alloy is shown in bar graph form in Figures 75 and 76. The influences of the two coating processes on the alloy strength were essentially equivalent, each affecting a strength reduction of approximately 10-15% in the room temperature and 2500°F properties, and a 20% reduction in the 2000°F properties. Both coating processes produced a moderate increase in alloy ductility at room temperature and 2500°F, and a significant, although not detrimental, reduction in ductility at 2000°F. D-43 alloy, as well as most other columbium base alloys, exhibits a strain aging behavior in the temperature range 1000-2000°F. Accompanying this phenomenon is an attendant region
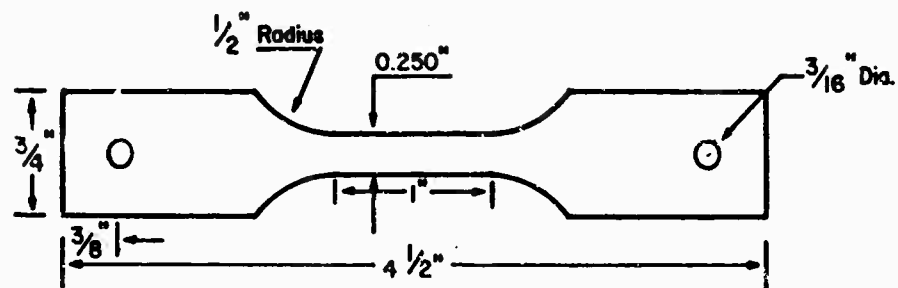
A. TENSILE SPECIMEN - RT to 2300°F
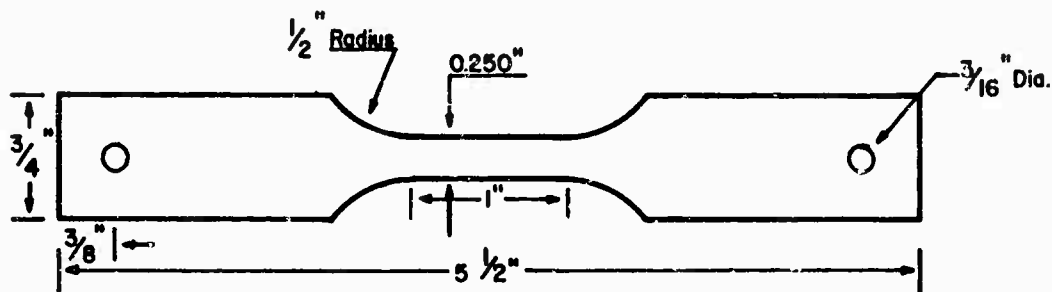
B. TENSILE SPECIMEN - 2500 and 2600°F
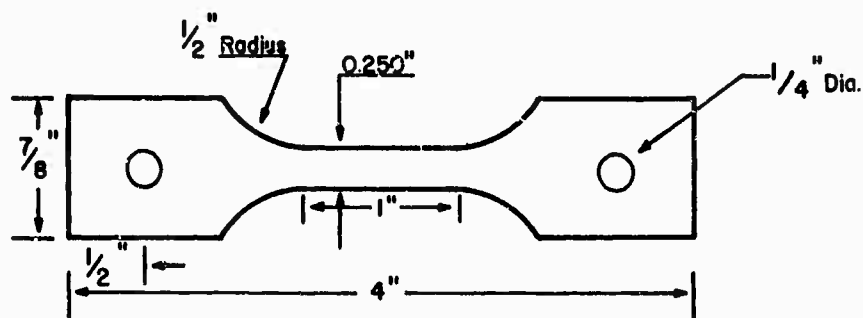
C. CREEP SPECIMEN - 2000 to 2600°F

Figure 74 Tensile and Creep Specimen Designs for Mechanical Property
Tests.

141

TABLE 25

Room Temperature Tensile Properties of 30 Mil D-43 Alloy Sheet -
Uncoated, Coated (Pack and Slurry), and After Coating Removal[1]

Coated Condition	U.T.S. psi	0.2 Offset Y.S. psi	% Elong. in 1" Gage	% R. A.
Uncoated	80,100	60,000	21.1	46.5
	81,900	64,300	27.5	53.8
As Cr-Ti Coated (Pack)	75,000	53,100	23.1	67.4
	74,000	52,100	26.9	71.0
Cr-Ti Coated (Pack)-	80,800	54,100	27.2	49.5
Coating Removed	77,500	52,100	28.1	42.4
As Cr-Ti-Si Coated (Pack)	72,300	50,900	24.4	71.5
	72,300	51,100	22.9	70.3
	72,600	52,100	26.8	67.9
Cr-Ti-Si Coated (Pack)-	70,700	49,800	24.8	73.0
Coating Removed	68,300	47,500	28.9	70.9
	67,700	47,200	30.4	77.4
As Cr-Ti-Si Coated	72,900	51,400	25.3	55.3
(Slurry)	72,300	50,700	27.0	67.0
	72,800	51,800	25.4	51.3

(1) MAB tensile test specifications - Reference (10)

142

TABLE 26

Tensile Properties of 30 Mil D-43 Alloy Sheet at 2000 and 2500°F
Uncoated, Coated (Pack and Slurry), and After Coating Removal[3]

Test Temperature	Coated Condition	U.T.S. psi	0.2 Offset Y.S. psi	% Elong. in 1" Gage	% R.A.
2000°F	Uncoated[1]	41,000	37,600	19.1	83.4
		40,900	37,900	18.7	77.6
	As Cr-Ti Coated[1] (Pack)	35,700	32,100	18.6	78.6
		35,200	31,100	22.4	74.0
	Cr-Ti Coated[1] (Pack) - Coating Removed	32,500	29,000	21.2	91.9
		31,700	28,700	21.6	92.0
	As Cr-Ti-Si Coated[2] (Pack)	31,700	28,400	13.5	8.0
		32,400	29,100	11.5	9.7
		33,000	28,900	8.3	8.6
	Cr-Ti-Si Coated[1] (Pack) - Coating Removed	31,900	27,800	18.3	89.3
		32,100	27,900	18.1	85.2
	As Cr-Ti-Si Coated[2] (Slurry)	32,300	28,000	17.4	27.4
		32,700	28,700	19.0	29.6
		33,000	29,400	18.4	30.0
2500°F	Uncoated[1]	19,600	17,700	41.1	93.1
		19,000	17,400	44.6	92.3
	As Cr-Ti-Si Coated[2] (Pack)	17,200	15,000	94.5	73.0
		17,700	15,600	81.4	77.2
		17,600	15,300	85.3	76.5
	As Cr-Ti-Si Coated[2] (Slurry)	17,800	15,600	61.9	80.7
		16,400	13,900	76.3	76.5

(1) Tested in vacuum - < 0.1 micron pressure
(2) Tested in air - one atmosphere
(3) MAB tensile test specifications - Reference (10)

143
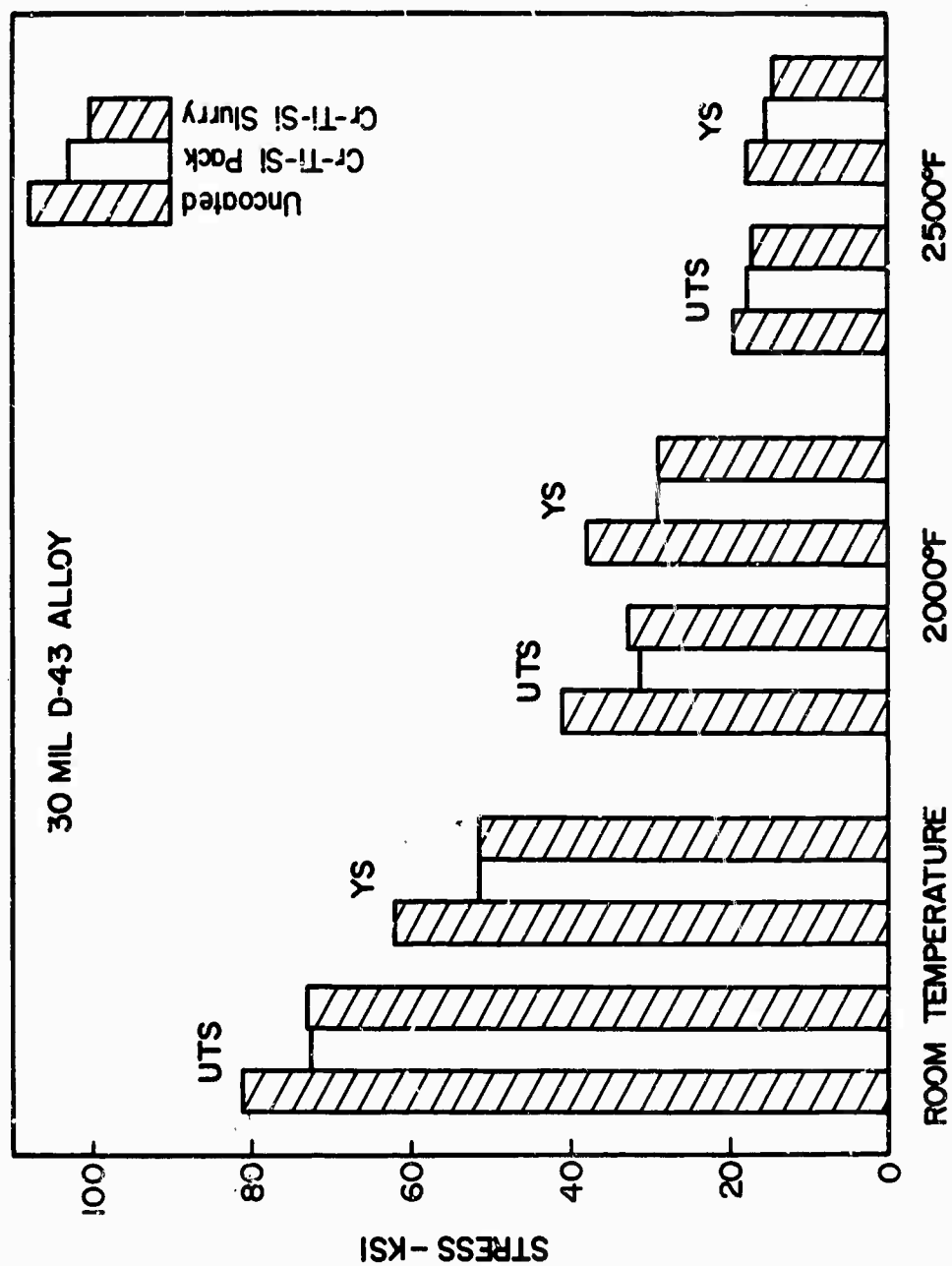
Figure 75   Tensile Properties of 30 Mil D-43 Alloy Sheet at Room Temperature, 2000 and 2500°F – Uncoated and Slurry and Pack Cr-Ti-Si Coated
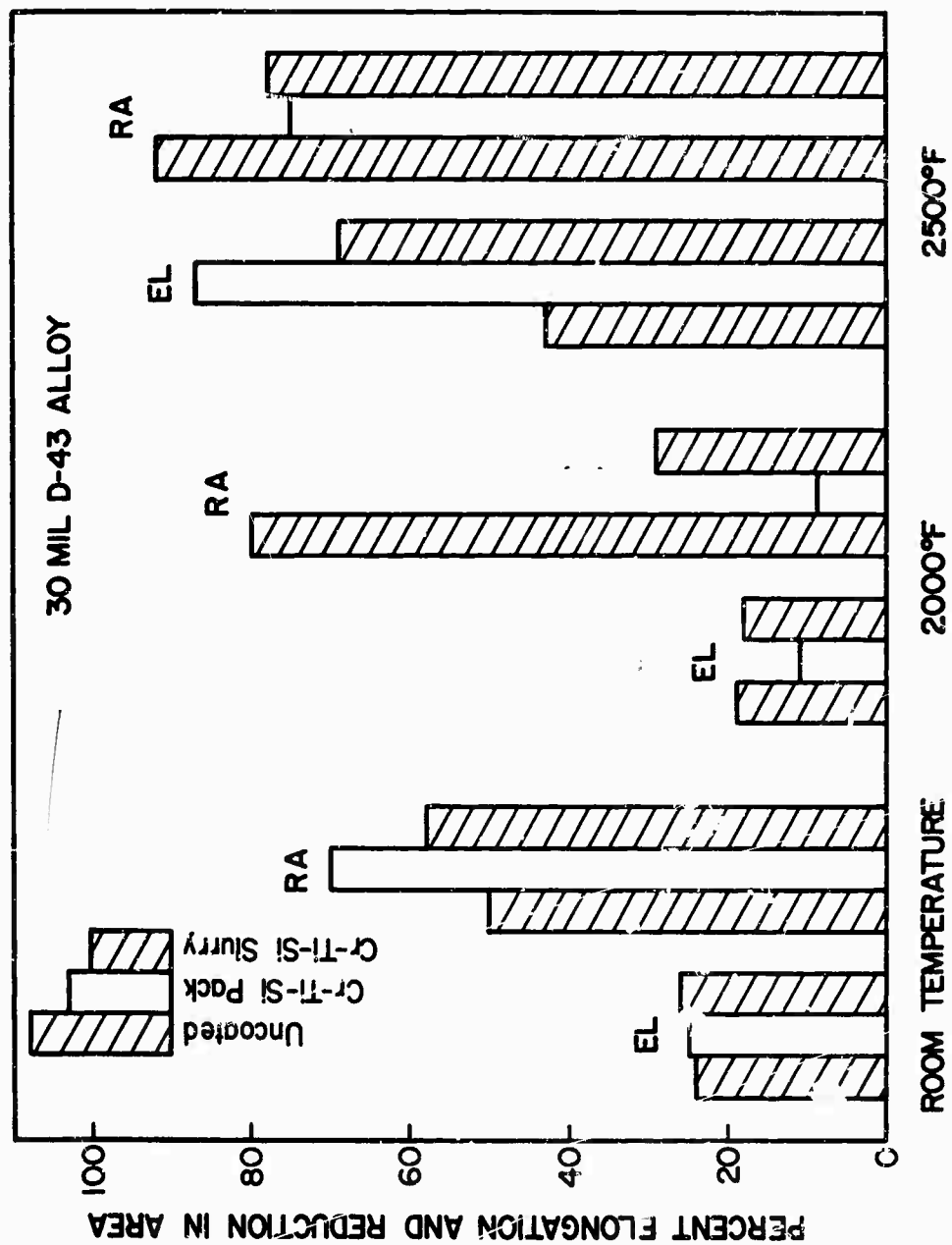
Figure 76 Tensile Properties of 30 Mil D-43 Alloy Sheet at Room Temperature, 2000 and 2500° F -
Uncoated and Slurry and Pack Cr-Ti-Si Coated

145

of minimum ductility[12]. The enhanced loss of ductility produced by the protective coating is associated with a localization of tensile strain at the base of cracks which initiate in the brittle surface layer. The localized exhaustion of ductility results in an accelerated fracture propagation.

Figures 77 and 78 are bar graphs displaying the influence of the pack Cr-Ti-Si coating process on the basic tensile properties of 30 mil D-43 alloy sheet. Regarding the room temperature properties, the Cr-Ti coating produced a 10-15% reduction in apparent strength, with no significant change in substrate ductility. No further strength reduction resulted from the subsequent siliconizing cycle, and removal of either the Cr-Ti or Cr-Ti-Si coatings was of little consequence.

Considering the 2000°F properties, the Cr-Ti coating cycle again affected approximately a 10% reduction in apparent strength, and the siliconizing cycle an additional 10% loss. The presence of the Cr-Ti coating had no influence on the composite ductility at 2000°F, thus the Laves phase was apparently quite ductile at this temperature. The presence of the Cr-Ti-Si coating reduced the substrate elongation approximately 50%, and this loss of ductility was restored by removal of the brittle silicide layer. Referring to Table 26, the influence of the silicide coating on fracture initiation and propagation is clearly shown by the very low reduction of area of the Cr-Ti-Si coated material. The reduction in the strength of D-43 alloy resulting from the application of the Cr-Ti-Si coating was undoubtedly associated with the gettering sink for both oxygen and carbon provided by the coating constituents. D-43 alloy is strengthened by oxide and carbide precipitation. The strong affinity of titanium and silicon for the interstitials apparently resulted in a reduction of the alloy hardening constituents, and the subsequent loss of strength and increase in ductility.

6.4.2 Creep Properties

Creep tests were performed with pack and slurry Cr-Ti-Si coated D-43 alloy specimens in air at 2000 and 2500°F. Two stress levels were investigated at each temperature with the intention of evaluating creep levels of approximately 1 and 5%. The test parameters and creep data are presented in Table 27. Room temperature tensile tests were also conducted on these specimens following the stress-oxidation exposure, and these data are also given in Table 27.

In general the slurry coated D-43 alloy sheet exhibited a slightly higher creep rate than the pack coated material. There was no visual evidence of coating failure on any of the sixteen specimens tested, even with as much as 5% creep in 50 hours at 2000°F.

146
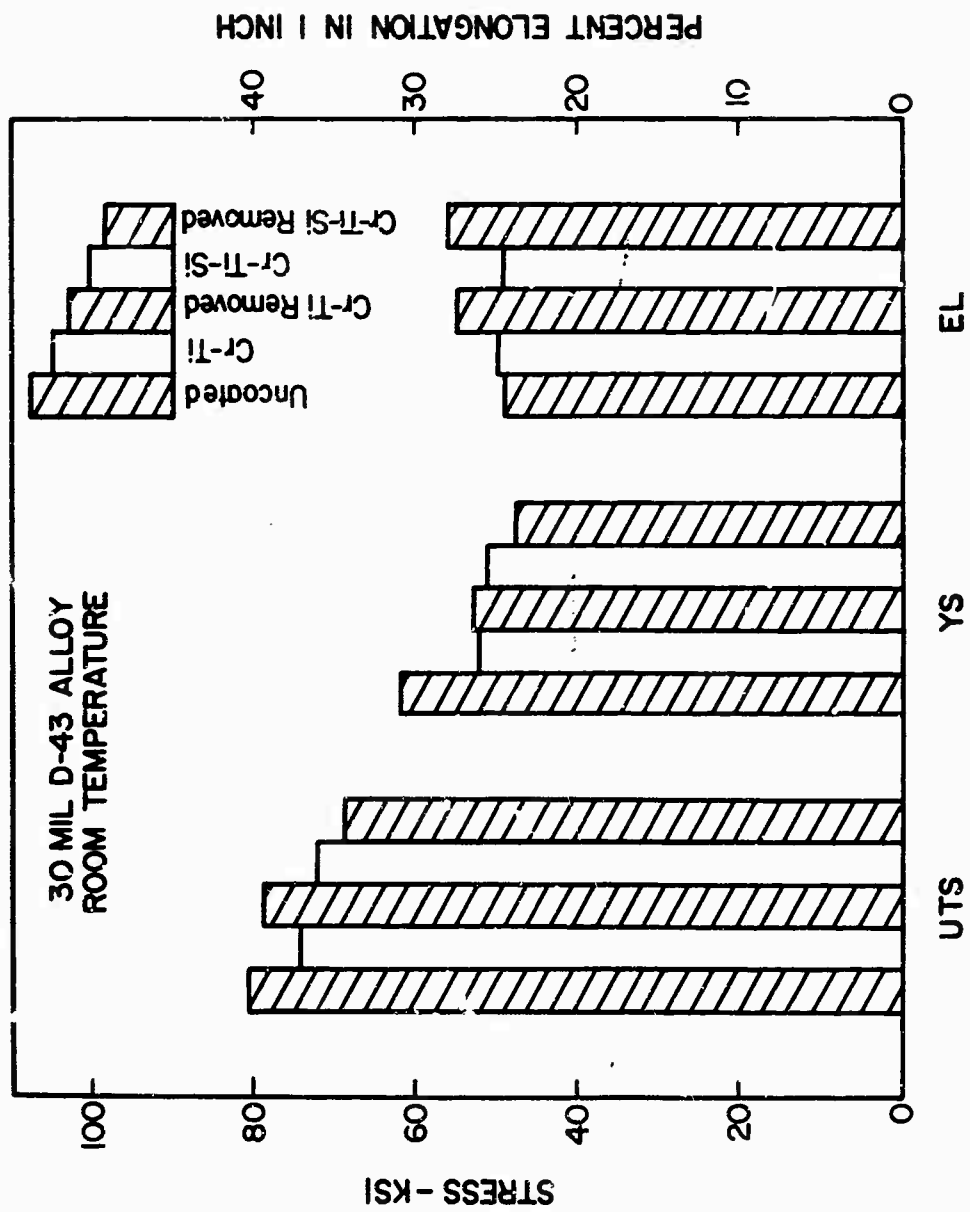
Figure 77 Room Temperature Tensile Properties of 30 Mil D-43 Alloy Sheet - Uncoated, Coated (Pack) and After Coating Removal

147
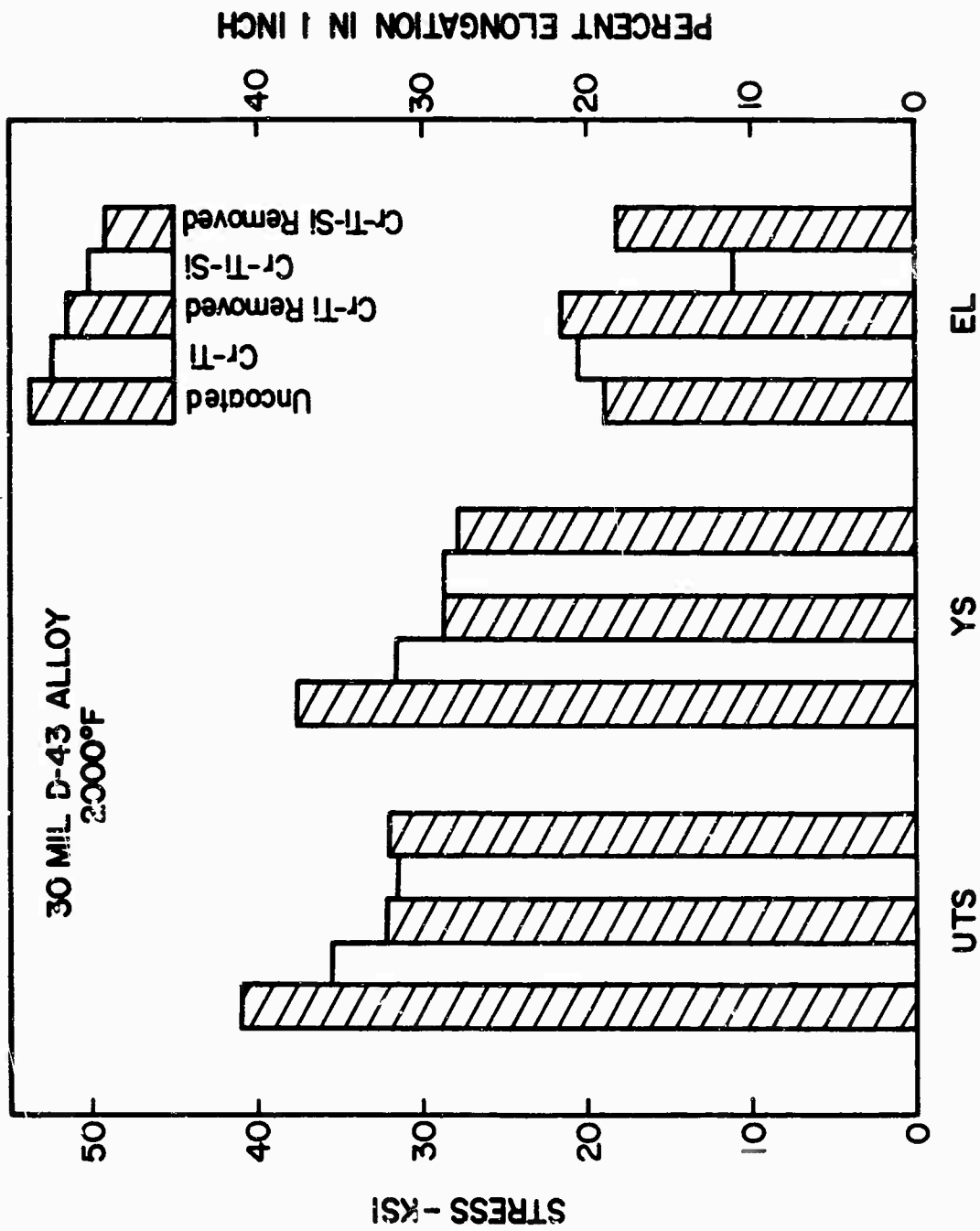
Figure 78 2000°F Tensile Properties of 30 Mil D-43 Alloy Sheet - Uncoated, Coated (Pack) and After Coating Removal

TABLE 27

Room Temperature Tensile Properties of Pack and Slurry Cr-Ti-Si Coated D-43 Alloy Sheet (30 Mil) After Various Creep Test Exposures

Cr-Ti-Si Coating Method	Creep Test Parameters[1]				Tensile Properties			
	Temp. °F	Stress (psi)	Hours Exposed	Creep % Elong.	U.T.S. psi	0.2 Offset Y.S. psi	% Elong. in 1" Gage	% R.A.
Pack	2000	8,500	100	0.5	72,400	51,300	24.2	72.1
		8,500	100	0.9	71,200	50,600	25.2	74.2
Slurry	2000	8,500	100	1.8	68,900	50,500	23.4	64.3
		8,500	100	1.3	68,900	48,900	21.2	73.3
Pack	2000	15,000	50	3.8	70,300	49,200	24.3	74.2
		15,000	50	4.0	68,400	47,700	22.1	68.8
Slurry	2000	15,000	50	5.3	67,300	47,200	22.7	75.4
		15,000	50	5.0	67,700	46,900	23.9	66.3
Pack	2500	2,000	50	1.9	71,700	55,100	19.9	71.9
		2,000	50	2.3	71,400	54,900	19.4	73.1
Slurry	2500	2,000	50	2.6	66,100	51,400	21.5	85.9
		2,000	50	2.3	66,300	51,500	21.1	76.9
Pack	2500	3,000	50	5.0	71,700	54,900	20.2	75.3
		3,000	50	5.2	70,800	53,300	23.2	66.1
Slurry	2500	3,000	50	6.0	63,400	48,800	19.2	74.9
		3,000	50	4.0	65,700	50,500	22.0	65.7

(1) Creep tested in air

149

A comparison of the room temperature tensile properties of the stress-oxidized material with the properties of as-coated D-43 sheet (Table 25) indicates essentially no change in properties as a result of the creep exposure. The slightly lower strength values obtained with the creep tested specimens is essentially the result of using original substrate dimensions for the stress calculations. The relative reduction in substrate cross-section associated with the creep extension is quite consistent with the apparent loss of composite strength. Also, the strength of the slurry coated material was slightly lower than that of the pack coated sheet, both before and after creep testing, thus accounting for the slightly higher creep rate evidenced by the slurry coated sheet. The unaltered tensile properties of the creep tested material is conclusive evidence of the complete protection provided by both the pack and slurry applied Cr-Ti-Si coatings.

6.5 Hot Gas Erosion Tests

Hot gas erosion tests were performed on several Cr-Ti-Si coated columbium alloy specimens utilizing a 40 KW Thermal Dynamics arc plasma facility. A simulated air mixture of 80% N_2-20% O_2 was introduced into the plasma gun, providing a hot gas velocity of approximately 1100 feet per second. Tests of 1/2 and 1 hour duration were conducted at temperatures from 2500 to 3100°F. The following heat flux conditions were encountered:

Temperature - °F	Heat Flux - Btu/ft²/sec
2500	400
2700	425
2800	460
2900	475
3050	520
3100	540

The Cr-Ti-Si coated specimens were curved sheet configurations fabricated from D-43, Cb-752 and B-66 alloy materials. The coating application parameters were as follows (retort - 3" diameter x 8" high):

Pack Composition	Activator w/o KF	Temperature °F	Time- Hours	System Pressure-mm
60Cr-40Ti	0.5	2340	12	1.5
Si	1.0	2100	6	10^{-2}

These processing parameters are those which would be employed in the coating of re-entry vehicle leading edge sections, gas turbine hardware, etc. In other words, the time-temperature conditions were somewhat more severe than those generally used in applying coatings on thin gauge sheet materials. The Cr-Ti coating overlay and diffusion zone thicknesses were approximately 1.0 and 1.2 mils respectively, and the Cr-Ti-Si coatings approximately 2.6 mils on each alloy.

150

Figures 79 and 80 are photographs showing the flame tested specimens and corresponding test parameters. Based on 1/2 hour exposures, the ease of protection was in the descending order D-43, B-66 and Cb-752. Coating failure occurred in less than 1/2 hour at 3100°F with D-43 alloy and at less than 1/2 hour at 2900°F with Cb-752 and B-66 alloys, in each case resulting in melting of the columbium oxide and rapid slag corrosion.

A Cr-Ti-Si coated D-43 specimen was exposed for 1 hour in the plasma flame at 3050°F without evidence of failure. Photomacrographs of the D-43 specimens exposed at 3050°F are shown in Figure 81. A very glassy oxide phase is observed in and around the center of the flame impingement area; and some erosion of the apparently soft glass phase was evident after 1 hour at 3050°F. Photomicrographs from sections through the latter specimen are shown in Figure 82. The exposed coating is considerably thinner in the center of the flame impingement area than in adjacent areas, indicating that some erosion of the oxidation products had occurred. It is also evident that the majority of the coating in this area had reacted with oxygen, leaving an amophorous-like oxide layer on the outer surface. A maze of cracks is observed in the microstructures taken from the flame fringe area. The relative thickness of the inner coating layer, which grew by diffusion during the arc plasma exposure, reflects the temperature gradient which existed from the center of flame impingement area outward.

The specimens which did not fail during the arc plasma exposure were subsequently cyclic oxidation tested in air at 2500°F. These data are summarized in Table 28. Plasma flame exposure at temperatures to 2900°F for times of 1/2 to 1 hour produced no serious degradation of the 2500°F protective properties of the Cr-Ti-Si coating. Only a few conditions were evaluated, and very little can be concluded regarding the degree of coating degradation which might be anticipated from a more severe plasma flame exposure. However, these data do demonstrate the higher temperature capabilities of the Cr-Ti-Si coating on columbium base substrates, and also the influence of substrate composition on the relative behavior of the coating system at the very high temperatures.

7. Cr-Ti-Si COATINGS ON TANTALUM BASE MATERIALS

The isomorphous resemblance of the Cb-Cr-Ti-Si and Ta-Cr-Ti-Si systems suggests that the Cr-Ti-Si coating might provide at least equivalent oxidation protection on both columbium and tantalum base substrates. Also, the higher melting point of tantalum oxide ($\sim 3450°F$), in comparison with columbium oxide ($\sim 2700°F$), suggests an even higher temperature use potential of the Cr-Ti-Si system on tantalum. However, previous cursory analysis of the Cr-Ti-Si coating on tantalum materials have indicated this is not the case. The poorer protective performance has been attributed in part to the slower diffusion of chromium and titanium in the tantalum matrix, in contrast to columbium, and an attendant absence of the required oxidation resistant solid solution region (diffusion zone) beneath the Cr-Ti-Si overlay. Titanium precoating the tantalum material prior to application of the Cr-Ti-Si coating greatly improved the performance of the coating system, which corroborates this latter suggestion.
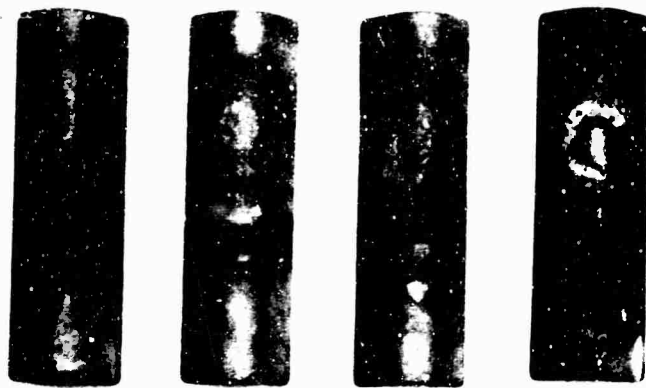
151

2500° F   2700° F   2800° F   2900° F
1/2 Hour   1/2 Hour   1/? Hour   1/2 Hour
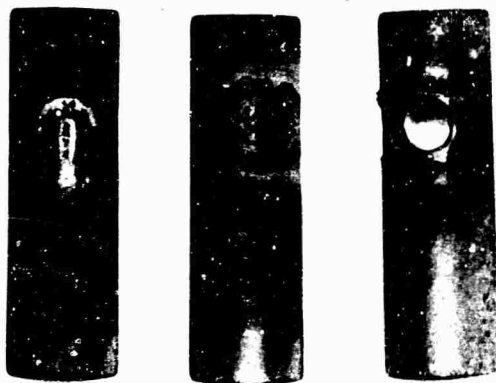
3050° F   3050° F   3100° F
1/2 Hour   1 Hour   20 Secs.

Figure 79 Cr-Ti-Si Coated D-43 Specimens After Exposure in Hot Gas Plasma
           Flame   1X
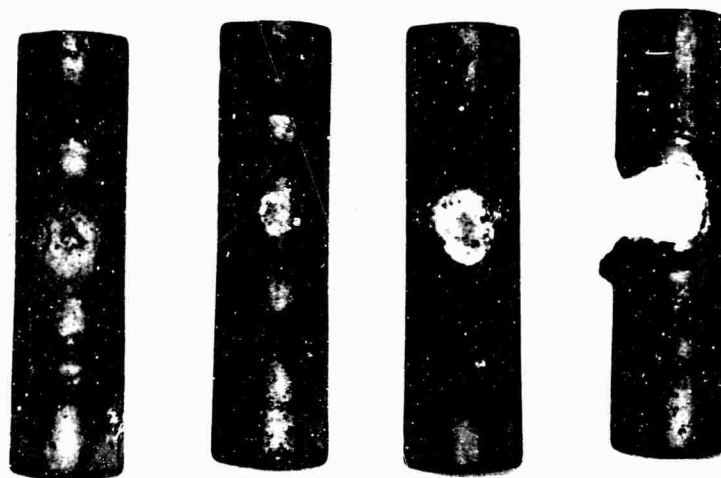
2500°F   2700°F   2800°F   2900°F
1/2 Hour   1/2 Hour   1/2 Hour   15 Secs.

Cb-752 Alloy

2800°F   2900°F
1 Hour   10 Minutes

B-66 Alloy

Figure 80   Cr-Ti-Si Coated Cb-752 and B-66 Alloy Specimens After Exposure
             in Hot Gas Plasma Flame   1X

153

3050° F
1 Hour

3050° F
1/2 Hour

Figure 81   Photomacrographs Showing Flame Impingement Area on Arc Plasma
Tested Cr-Ti-Si Coated D-43 Alloy
5X

154

Center   Near Edge   Far Edge

Flame Impingement Area

Figure 82 Photomicrographs from Arc Plasma Tested Cr-Ti-Si Coated D-43 Alloy - 1 Hour - 3050°F 500X

TABLE 28

Protective Properties of Cr-Ti-Si Coating at 2500°F
After Pre-Exposure in Arc Plasma Flame

| Substrate | Arc Plasma Test | | Protective Life at |
	Time – Hours	Temperature – °F	2500°F – Hours(a)
D-43	1/2	2500	>180
	1/2	2700	>180
	1/2	2800	150
	1/2	2900	72
	1/2	3050	(b)
	1	3050	(b)
Cb-752	1/2	2500	>180
	1/2	2700	>180
	1/2	2800	120
B-66	1	2800	>180

(a) Post oxidation – after plasma test

(b) Sectioned for metallography – no further test

156

Only a very brief study of the Cr-Ti-Si coating on tantalum was conducted in this program. The purpose of this effort was to merely demonstrate the capabilities of the system on tantalum, utilizing the processing parameters developed for application of the coating on columbium. Several processing sequences were employed in preparing these specimens, representing both the conservative conditions utilized in coating thin gauge aerospace sheet materials and the higher temperature - longer time parameters employed in coating gas turbine vanes, leading edge components, etc.

Table 29 lists the cyclic oxidation test data and the coating application parameters for Cr-Ti-Si coatings applied on unalloyed tantalum, Ta-10W and D-43 (for comparison) alloys. These data indicate that the Cr-Ti-Si coating is less protective on tantalum base substrates than on columbium materials, although very useful and promising protective lives were achieved. In comparing unalloyed tantalum and Ta-10W, at 1800°F the Ta-10W alloy was more difficult to protect, whereas at 2500°F the reverse trend was evidenced. Figures 83 and 84 present photomicrographs comparing identically processed Cr-Ti and Cr-Ti-Si coatings on Ta, Ta-10W and D-43 alloy. The relatively less pronounced diffusion of coating elements in the tantalum matrix, in comparison with columbium, is apparent in the microstructures.

8. COATINGS FOR TEMPERATURES ABOVE 2700°F

In keeping with the growing need for materials with increasingly higher temperature capabilities, a trend is evident in the aerospace industry to exploit the strength potential of columbium and tantalum base materials at temperatures above 3000°F. The Cr-Ti-Si coating system has demonstrated excellent protective properties on columbium base materials at temperatures up to 2700°F, and useful lives have been realized at temperatures to 3100°F. However, two characteristics of the Cr-Ti-Si system which are integral to its outstanding performance under most environmental conditions are, in fact, limiting factors to its utilization under certain other conditions. The relatively low softening po. t of the oxide which forms on the coating surface is effective in providing the Cr-Ti-Si coating with a selfhealing capability at temperatures above approximately 2300°F. However, melting of this oxide ultimately establishes a temperature limit at which the coating is protective, and this upper limit appears to be in the vicinity of 3100-3200°F. Secondly, the presence of chromium in the coating system is a deterrent to its utilization in high temperature-reduced pressure environments, owing to the ease with which the chromium is vaporized from the coating alloy.

Two approaches were considered in an attempt to up-grade protective coating systems for columbium: (1) modification of the existing Cr-Ti-Si system, and (2) a barrier layer approach. Modification of the Cr-Ti-Si system essentially involved efforts to alloy the silicide layer with high melting point constituents such as W, Mo. V, etc., by the addition of these elements to the silicon coating pack. It was speculated that upon exposure in air at elevated temperatures an oxidation product would

157

TABLE 29

Protective Life of Cr-Ti-Si Coating on Tantalum Base Substrates

Process[a] Designation	Alloy		Protective Life - Hours	
			2500°F	2700°F
A	Ta	72, >168(9)	48,50,50,56,72	-
	Ta-10W	4,2,4,4,4,4,4 4,4,4	7,54,56,72,54 72,72,78,78,78	-
	D-43(b)	>168(10)	72,72,72,72,78 96,168	-
B	Ta	>240(4)	48,51,72,72	16,20
	Ta-10W	5,6	48,72,72,72	18,20
	D-43	>240(3)	120,125,128,216,240,247	16,25,33,36
C	Ta	>240(3)	24,24,26,51	8,11
	Ta-10W	192,192	51,55,72,75	11,12
	D-43	>240(3)	96,96,120,128,145,145	19,23,32,48
D	Ta	>240(4)	72,72,100,145	12,13
	Ta-10W	6,7	72,72,72,77	14,14
	D-43	>240(3)	100,145,145,168 168,168	39,44,54,54

(a) Process	Pack Composition	Time-Hours	Temperature-°F	Pressure-mm
A	50Cr-50Ti	8	2300	1.5
B	60Cr-40Ti	16	2300	1.5
C	50Cr-50Ti	8	2350	1.5
D	50Cr-50Ti	16	2350	1.5
Siliconizing	Si	6	2100	10^{-2}

(b) D-43 alloy - Cb-10W-1Zr - For comparison

158
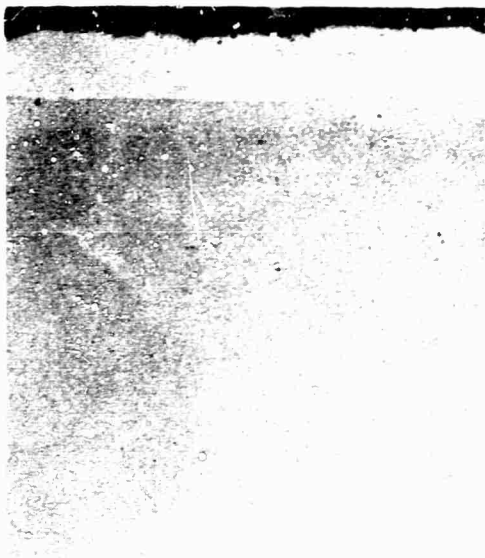
Ta-10W   Unalloyed Ta

D-43

Figure 83   Microstructures of Cr-Ti Coatings on Ta, Ta-10W and D-43 Alloys-
            Process Conditions - D   500X
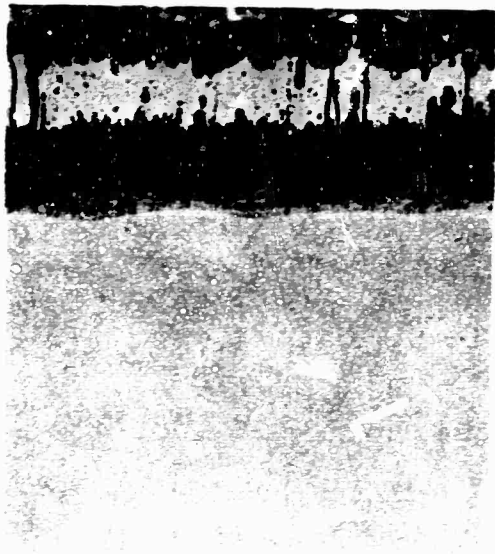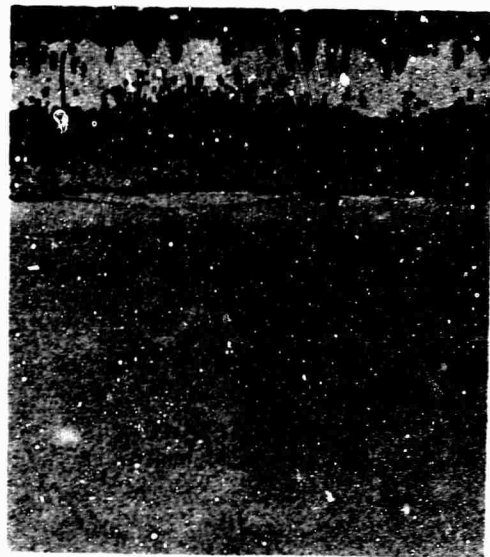
Ta-10W   Unalloyed Ta

D-43

Figure 84 Microstructures of Cr-Ti-Si Coatings on Ta, Ta-10W and
D-43 Alloys - Process Conditions - D   500X

160

form on the modified coating surface which was more refractory than that formed on the basic Cr-Ti-Si system. The presence of these higher melting point elements might also serve to deter the diffusion and ultimate vaporization of chromium from the coating in both one atmosphere and reduced pressure environments.

The alternate approach to the problem, the barrier layer concept, was expected to provide coating systems which would exhibit a still higher temperature capability than that attainable by modification of the Cr-Ti-Si coating. The procedure in this case was to initially form a diffusion barrier layer of tungsten or molybdenum on the columbium surface by diffusion alloying or chemical vapor deposition. The surface of the barrier layer was subsequently alloyed with Si-(W) to form an oxidation resistant disilicide coating. The interposed barrier layer was thus diffusion bonded to both the protective silicide coating and to the columbium substrate. The barrier layer would serve to inhibit the diffusion of coating elements inward and substrate elements outward during oxidation exposure. Advantage was taken here of the protective coating systems developed for tungsten and molybdenum under Contract AF 33(616)-8188[1]. Coatings developed under the above contract have effectively protected tungsten base materials at temperatures in excess of 3500°F. The rate of diffusion of columbium outward and of the coating elements inward through the barrier layer would essentially control the life of the system. The absence of chromium in these systems would also render the coating more attractive for utilization under reduced pressure conditions.

In conjunction with this development work on columbium, a parallel coating effort was also conducted with tantalum base materials. The much higher melting point of tantalum oxide ($\sim$3450°F)[2] relative to that of columbium oxide ($\sim$2700°F)[2], and the otherwise chemical similarity of the two refractory metals, suggests that the coatings developed for columbium might exhibit improved high temperature properties when applied on tantalum base materials. Localized failure of a protective coating on columbium, at temperature above $\sim$2600°F, results in catastrophic destruction of the system by the molten oxide slag. A significant margin of safety regarding catastrophic failure is available with a tantalum base substrate.

Since there were a large number of coating systems evaluated in this work, and since it involved both single and co-deposition of various coating elements, a consistent nomenclature was developed for expressing the coating systems. Letting X, Y and Z represent three different coating elements, the symbols written in the following forms are defined as follows:

    X - Elemental deposition of X from a pure X pack
(X+Y) - Co-deposition of X and Y from prealloyed (X+Y) pack
  Z(Y) - Co-deposition of Z and Y from a Z pack containing minor
        additions of Y

161

The order in which the symbols are written is consistent with the order
in which the coating cycles were performed.

8.1 Modification of Cr-Ti-Si System

Initially one series of coating runs was made to investigate various
alloy additions to the Cr-Ti-Si system. Only D-43 alloy sheet coupons were
used in this work, and all coatings were pack applied in a 3" diameter x 8"
high retort. Eight sets of coupons were initially Cr-Ti coated using the
following processing parameters:

        (a)   Pack - 60Cr-40Ti

        (b)   Activator - 0.5 w/o XF

        (c)   Temperature - 2300°F

        (d)   Time - 8 hours

A photomicrograph showing the Cr-Ti alloy coating and metallographic measure-
ments is presented in Figure 85.

Figure 86 is a schematic diagram describing the processing parameters and
the eight modified coating systems obtained by variations in the pack siliconi-
zing cycle. Three additives were made to the Cr-Ti-Si system: tungsten,
molybdenum and vanadium. Tungsten and molybdenum powders (-250 mesh) were
added to the granular silicon pack (-8 +30 mesh) in the amount of 4 w/o.
Two basic processing treatments were followed in forming the tungsten and
molybdenum modified coatings: (1) 6 hours at 2100°F representing the
siliconizing parameters normally utilized in forming the Cr-Ti-Si system
on columbium, and (2) 4 hours at 2200°F representing the siliconizing para-
meters developed for the formation of the Si-(W) coating on tungsten[1].
Each of these coating cycles included a 1 hour hold at 1500°F in accordance
with the parameters developed in the work of Nolting and Jefferys[1].
Coatings formed by siliconizing in pure silicon packs were prepared as
standards of comparison. The Si-(V) modification was obtained with a
60 w/o Si-40 w/o V pack of -8 +30 mesh metallic granules. The eighth
coating system represents an effort to thoroughly alloy the outer surface
of the silicide with tungsten by diffusion treating the (Cr+Ti)-Si coated
D-43 alloy coupons in a pure tungsten powder pack. All of the siliconizing
packs were activated with a halide mixture of 1.0 w/o NaF + 0.5 w/o KF.
Figures 87 and 88 are photomicrographs showing the microstructures of these
coatings.

The differences in the microstructures of the various modified coatings
were generally not significant, however, a couple of points should be noted.
In comparing the W and Mo modified coatings with the unmodified Cr-Ti-Si
coatings, a greater retention of the original titanium enriched substrate
region (diffusion zone) and precipitated Laves phase is evident in the modified

162
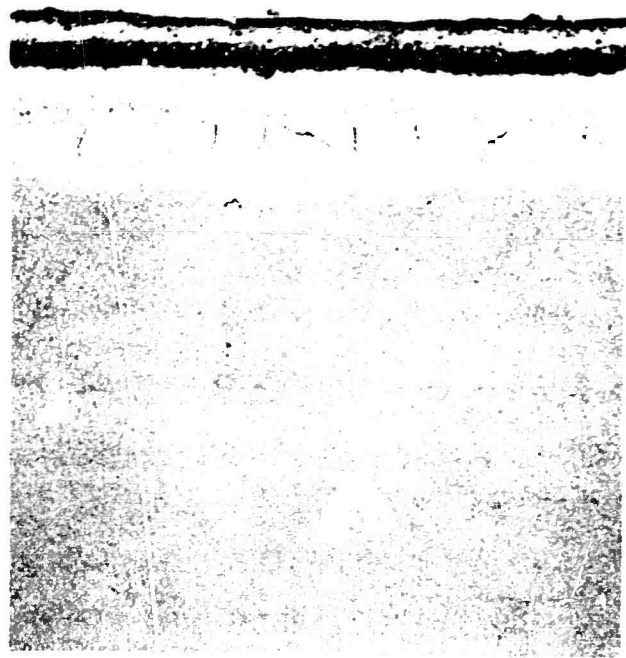
1.2 Mils - Overlay

1.2 Mils - Diffusion Zone

Subst.ate

Figure 85   Photomicrograph of Cr-Ti Coating on D-43 Alloy Prior to
Siliconizing in Modified Silicon Packs   250X

163
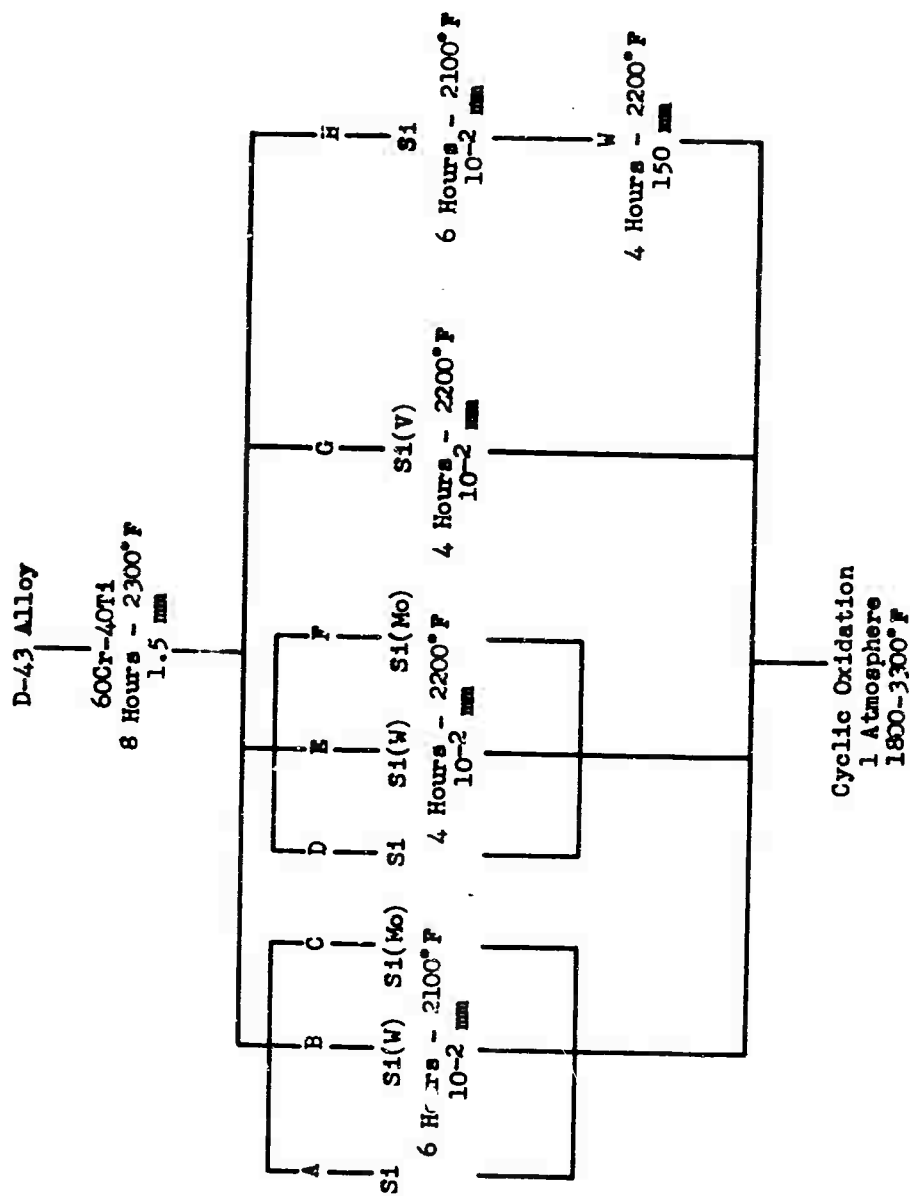
Figure 86 Schematic Showing the Eight Modified Cr-Ti-Si Coating Systems Evaluated on D-43 Alloy
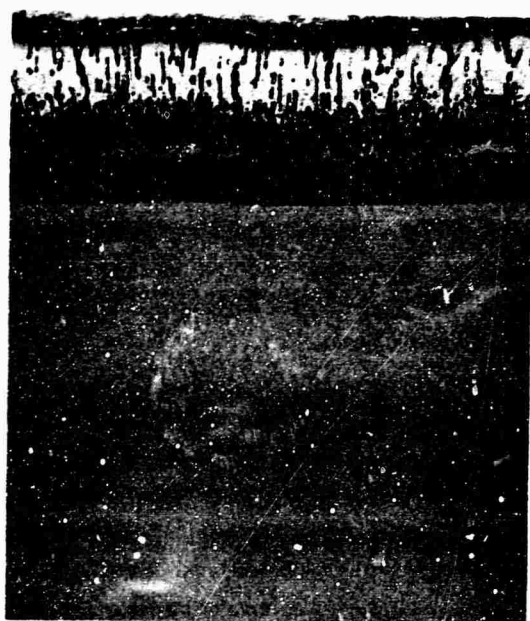
A   (Cr+Ti)-Si   B   (Cr+Ti)-Si(W)
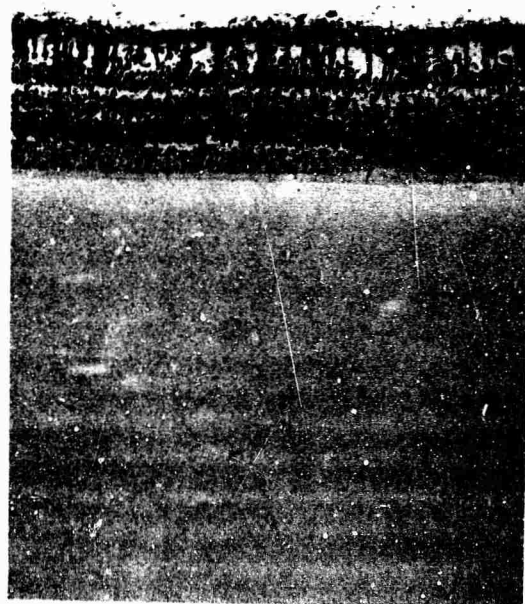
C   (Cr+Ti)-Si(Mo)   D   (Cr+Ti)-Si

Figure 87   Photomicrographs of Modified Cr-Ti-Si Coatings on D-43 Alloy -
See Figure 86 for Coating Parameters   250X

165

E   (Cr+Ti)-Si(W)   F   (Cr+Ti)-Si(Mo)
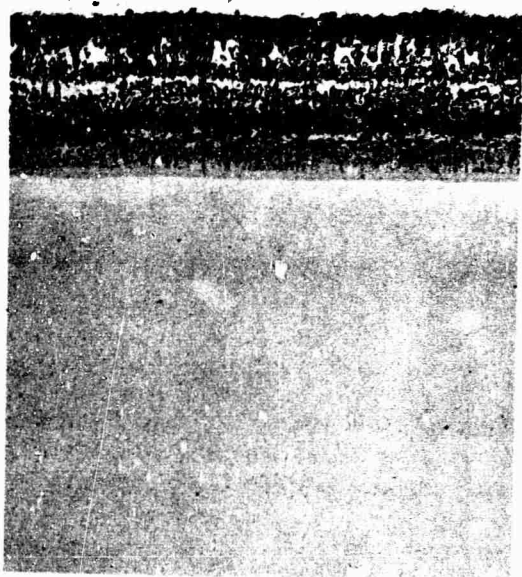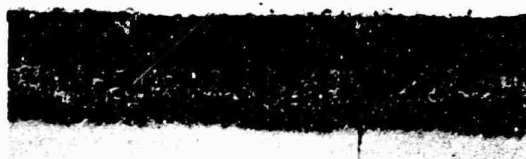
G   (Cr+Ti)-Si(V)   H   (Cr+Ti)-Si-W

Figure 88   Photomicrographs of Modified Cr-Ti-Si Coatings on D-43 Alloy
See Figure 86 for Coating Parameters   250X

coatings. The silicon diffusion front appears to have penetrated to a lesser depth with the modified coatings, for comparable coating times and temperatures. Secondly, diffusion treating the Cr-Ti-Si coating in a pure tungsten pack (system H) resulted in a very porous layer on the surface of the silicide coating.

Cyclic oxidation tests were conducted with the modified Cr-Ti-Si coatings in air (one atmosphere) at temperatures from 1800 to 3300°F. Two replicate specimens were evaluated in most cases. These data are shown in Table 30, along with the metallographically measured overlay coating thicknesses. Prior to discussiong these data, however, a brief reference should be made to the oxidation test procedures. This information was given in Table 3. At test temperatures from 1800-3000°F the coated coupons were exposed in globar heated box furnaces. At 1800-2700°F the test coupons were supported on high purity Al_2O_3, however, at temperature above 2700°F reaction between Al_2O_3 and the protective coatings resulted in premature coating failures. Therefore, sacrificial molybdenum pads protected with the Si-(W) coating were utilized to support the test coupons at 3000°F and above.

For testing in the temperature range 1800-3000°F the thermal cycle involved air cooling of the coupons to approximately room temperature. The exposure interval between cycles decreased with increasing test temperature. This procedure was followed for improved accuracy in detecting the time of coating failure, since the protective lives of the coatings were consider- ably shorter at the higher test temperatures. It was observed that during exposure of these specimens at temperatures above 3000°F the columbium test coupons and molybdenum sacrificial pad became firmly bonded together by inter- diffusion of the oxidized coatings. Upon cooling to near room temperature the differential in thermal expansion between the two systems was sufficient to fracture the bond, and both coating systems were severely damaged. Failures attributed to this origin would obviously not be representative of the capabilities of the protective coatings. Thermal cycling from the 3100-3400°F test temperatures therefore involved cooling of the coupons to approximately 1000°F, although it was recognized that this less severe condition may have influenced the absolute protective lives exhibited by the coatings. The relative performance of the various coating systems should have been essen- tially unaffected by this condition. The tests at 3100°F and above were conducted in an induction heated ZrO_2 tube furnace, and continuous observation of the test coupons was possible with an optical pyrometer.

Returning now to Table 30, the overlay coatings ranged in thickness from 3-4 mils, with retained diffusion zones ranging from 0.4-0.9 mils. Only one specimen of the sixteen tested at 1800°F failed (5 hours) within the test duration time of 168 hours. The coating modification in this case was attained by diffusion treating the Cr-Ti-Si coating in a pure tungsten pack; and this system displayed extremely poor protective properties in all temperature ranges. The relative effects of the silicide modifications on the protective properties of the Cr-Ti-Si system are generally not signifi- cant in this group of data. Although the tungsten and molybdenum additions

167

TABLE 30

Metallographic Results and Cyclic Oxidation Protective Lives for
Modified Cr-Ti-Si Coatings on D-43 Alloy

Coating System Code[a]	Composition	Overlay Thickness Mils	Cyclic Oxidation Protective Life - Hours[b] 1800°F	2500°F	2700°F	3000°F	3100°F	3200°F	3300°F
A	(Cr-Ti)-Si	3.5-3.8	>168(2)(c)	72,78	3,32	1.0-4.0	2.0,2.25	0.12,0.25	0.17
B	(Cr-Ti)-Si(W)	2.9-3.0	>168(2)	102,>168	20,15	1.0,1.5	1.25,1.5	0.9,1.0	0.42,0.67
C	(Cr-Ti)-Si(Mo)	3.0-3.1	>168(2)	78,96	24,34	1.5-2.0	1.5,1.5	0.72,0.75	0.50
D	(Cr-Ti)-Si	3.0-3.2	>168(2)	78,78	10,25	1.0,3.0	1.5,1.5	1.25,1.70	0.75
E	(Cr-Ti)-Si(W)	3.5-3.6	>168(2)	72,120	14,27	0.5,2.5	3.0,4.0	1.0,1.1	0.25
F	(Cr-Ti)-Si(Mo)	3.9-4.0	>168(2)	96,120	24,25	2.5,2.5	1.75,2.5	1.8,2.0	0.08,0.2
G	(Cr-Ti)-Si(V)	3.1-3.3	>168(2)	54,72	18,27	1.5,2.5	1.5,3.25	0.5,0.5	0.12,0.42
H	(Cr-Ti)-Si-W	3.0-3.2	5,>168	54,72	1,12	0.5-0.5	0.25,0.25	0.25,0.25	0.22

(a) See Figure 86 for coating parameters

(b) See Table 3 for oxidation test procedures

(c) Denotes number of specimens

produced the individually most protective systems, the trend in protective performance was only slightly improved by the compositional modifications. Processing at 2200°F generally produced the more protective coatings, as did alloying of the silicide with tungsten. However, with this narrow differential in protective properties, and with the limited number of replicate tests, even general performance trends were difficult to ascertain.

The microstructures of the modified coatings formed in this initial effort exhibited no salient evidence that alloying was accomplished by the minor silicon pack additions. Thus, a second series of modified Cr-Ti-Si coated specimens were prepared using silicon pack additions of up to 50 w/o tungsten and molybdenum.

D-43 alloy was again employed as the substrate material, and the initial Cr-Ti coating was applied in 8 hours at 2300°F using a 60Cr-40Ti alloy - k. The siliconizing cycle was accomplished in 4 hours at 2200°F. Figure shows photomicrographs of the various tungsten modified coatings on D-/ alloy. The only significant influence of the pack addition on the microstructures of the resulting coatings was an increase in the porosity or second phase density near the coating surface with an increasing tungsten content in the pack. The reason for this porosity was not apparent.

The metallographic and cyclic oxidation test results obtained with these modified coatings are given in Table 31. Uniformly thick coatings were obtained with pack additions of up to 20 w/o, whereas the 50 w/o tungsten addition produced an extremely non-uniform coating ranging in thickness locally from 0.2-3.0 mils. The coating formed by siliconizing in the 50 w/o molybdenum pack was uniform, on the other hand, but unusually thick. Inhomogeneity of the mixed pack accounts for the thickness non-uniformity, but not for the exceptionally thick molybdenum modified coating.

The pack additions were not detrimental to the low temperature (1800°F) properties of the Cr-Ti-Si system, within the time limit of the oxidation exposure. However, a definite degradation of the 2500°F protective capabilities of the Cr-Ti-Si system was affected by the 20 and 50 w/o pack additions. At 2700°F the modified coatings were generally the more protective systems, particularly those coatings formed by siliconizing in the 50 w/o Mo pack (>45 hours). However, these longer protective lives can be attributed in part to the greater thicknesses of the modified coatings, particularly in the case of the latter system. For oxidation at 2800-3200°F the alloy modifications were generally ineffective in upgrading the protective performance of the Cr-Ti-Si coating. Protective lives of 6-15 hours were recorded at 2800°F and 0.1-0.9 hours at 3200 and 3300°F.

As with previous modified coatings, the alloy additions only sporadically improved the higher temperature capabilities of the Cr-Ti-Si coatings, and this improvement was not marked. Either insufficient modification of the silicide was accomplished to effect any temperature upgrading in the refractory

169

None   4 w/o W

Silicon Pack Addition

20 w/o W   50 w/o W

Silicon Pack Addition

Figure 89 Tungsten Modified Cr-Ti-Si Coatings on D-43 Alloy   250X

170

TABLE 31

Metallographic and Cyclic Oxidation Test Results for Modified
Cr-Ti-Si Coatings on D-43 Alloy

Coating System	Silicon Pack Addition(a)	Coating Thickness Mils	Protective Life - Hours(b)					
			1800°F	2500°F	2700°F	2800°F	2200°F	2300°F
(Cr-Ti)-Si	–	2.0-2.4	>146(2)	120,>146	3,5	9,8	0.2,0.9	0.1,0.2
(Cr-Ti)-Si(W)	4 w/o W	2.2-2.4	>146(2)	96,>146	9,10	8,6	0.3,0.8	0.5,0.6
(Cr-Ti)-Si(W)	20 w/o W	2.6-2.8	>146(2)	120,122	20,21	8,8	0.7,0.7	0.1,0.9
(Cr-Ti)-Si(W)	50 w/o W	0.2-3.0	>146(2)	25,74	16,21	2,8	0.2,0.9	0.1,0.1
(Cr-Ti)-Si(Mo)	20 w/o Mo	2.4-2.6	>146(2)	7,48	1,1	5,11	0.1,0.3	0.4,0.5
(Cr-Ti)-Si(Mo)	50 w/o Mo	4.0-4.6	>146(2)	32,48	>45,>45	15,>15	<0.1,2.3	<0.1,0.1

(a) Processing Conditions – 60Cr-40Ti – 8 hours – 2300°F – 10^{-2} mm
Si(W,Mo) – 4 hours – 2200°F – 10^{-2} mm

(b) See Table 3 for oxidation test procedures

171

properties of the silicide; or the high concentrations of chromium and/or titanium precluded any appreciable improvement in the high temperature properties of the system.

A final series of modified coatings were prepared to evaluate the relative effect of extreme differences in the concentrations of chromium and titanium on the oxidation performance of the modified coatings. Coupons were prepared by initially coating in packs of pure titanium, pure chromium and prealloyed 70Cr-30Ti and 60Cr-40Ti; and these various coatings were subsequently silicided in packs of pure silicon and Si-20 w/o W. Cb-752 was employed as the substrate material for this final series of coatings. The coating process parameters and oxidation test data are presented in Table 32.

The poorest oxidation performance was generally exhibited by the silicide coatings which were formed by initially processing in pure chromium or pure titanium packs. At test temperatures from 1800-2700°F the coatings formed in prealloyed Cr-Ti packs evidenced superior protective properties, however, this was not unexpected. At 3000°F the Ti-Si and Ti-Si-(W) coatings appeared to be the most protective, however, insufficient tests were run to establish any significant trend.

In general, the efforts to modify the refractory nature of the Cr-Ti-Si system for improved high temperature performance were unsuccessful. Although there were instances of definite improvement, the data were extremely inconsistent and no pronounced trends were evidenced. The dominant influence of the chromium and titanium in the coating undoubtedly dictates the overall oxidation characteristics of the system, regardless of the alloy modification. Also, the degree of alloying accomplished by the co-deposition was uncertain, and it may have been quite insignificant owing to the rapid growth rate of the disilicide phase. Based on this work, it appears that modification of the Cr-Ti-Si coating by the co-deposition of the silicon and modifiers (vacuum pack) has little merit. However, other methods may be devised, and the utilization of a duplex pack-slurry technique or an entirely slurry method may provide the means.

8.2 Barrier Layer Coatings

The concept of a diffusion barrier coating system was discussed in the introduction to Section 8. Tungsten and molybdenum were selected as the barrier layer metals, owing to their slow interdiffusion rates with columbium and tantalum[13]. Two techniques were investigated for the formation of diffusion barrier layers: (1) vacuum pack deposition and (2) chemical vapor deposition. It was recognized that by the pack method a solid solution region would be formed on the substrate surface, whereas a pure metal could be deposited by the chemical vapor deposition technique. For the purpose of a diffusion barrier layer the latter technique obviously offers distinct advantages.

172

TABLE 32

Cyclic Oxidation Test Results of Modified Cr-Ti-Si Coatings
on Cb-752 Alloy

Coating System[a]	Protective Life				
	Hours			Minutes	
	1800°F	2500°F	2700°F	3000°F	3200°F
Ti-Si(W)	2,48,71	2,2,4	1,1,1	11	2
Ti-Si	2,2,103	2,2,7	1,1,2	30	9
Cr-Si(W)	2,71,>120	5,5,7	1,1,1	3	2
Cr-Si	2,26,96	5,5,7	1,1,2	2	11
(70Cr-30Ti)-Si(W)	>120(3) [b]	48,48,95	1,2,2	4	8
(70Cr-30Ti)-Si	23,23,>120	23,52,71	3,3,4	4	1
(60Cr-40Ti)-Si(W)	>120(3)	71,79 >120	16,21,23	3	1
(60Cr-40Ti)-Si	>120(3)	26,71,71	2,2,6	1	1

(a) Processing conditions:

| Pack Composition-w/c	Activator-w/o	Time-Hrs.	Temperature-°F	System Pressure-mm
Ti	0.5 KF	6	1900	10^{-2}
Cr	0.5 NaF	8	2350	1.5
60Cr-40Ti	0.5 KF	8	2300	1.5
70Cr-30Ti	0.5 KF	8	2300	1.5
Si	1.0 KF	8	1800	10^{-2}
Si-20W	1.0 KF	8	1800	10^{-2}

(b) Denotes number of replicate specimens

173

8.2.1 Vacuum Pack Coating Technique

-Several attempts were made to form tungsten and molybdenum barrier
layers on columbium and tantalum base substrates by the vacuum pack process.
Coupons of three columbium base materials (unalloyed columbium, B-66 and
D-43 alloys) and Ta-10W alloy were imbedded in pure -250 mesh tungsten or
molybdenum powder packs containing 5-10 w/o NaF. Diffusion cycles of
6 hours at 2300°F and 6 hours at 2500°F were performed, at system pressures
of both 10^{-2} mm (continuous evacuation) and 150 mm (argon). Past experience
with the vacuum pack process had indicated that greater utilization of the
pack activator and generally higher rates of coating deposition are obtained
in static systems, as opposed to dynamic systems. The influence of system
pressure was found insignificant in these coating runs. Metallographic
examination indicated that the tungsten and molybdenum solid solution layers
formed on the substrate surfaces were nil for the 2300°F treatment, and were
quite thin (0.1-0.3 mils) even after 6 hours at 2500°F. Weight gains of up
to 7-8 mg/cm^2 were obtained with both the tungsten and molybdenum on columbium
as a result of the 2500°F diffusion treatment, whereas the Ta-10W alloy
coupons lost weight during this coating cycle. The reactivity of the tantalum
alloy with the halide activator was obviously quite significant. There was
microstructural evidence of substrate contamination in the columbium materials
after the diffusion treatments, and the morphology of the precipitate in the
matrix resembled that of carbides observed in columbium. The induction
heated susceptor in the coating furnace was graphite. Figure 90 shows
photomicrographs of the tungsten solid solution zones formed on the surface
of the columbium and tantalum base substrates at 2500°F.

An effort was also made to prealloy the surface of the four substrates
with titanium and vanadium, with the idea that upon subsequent diffusion
treatment in the tungsten or molybdenum pack the vanadium or titanium pre-
coat might enhance the diffusion of tungsten or molybdenum in the substrate
surface. However, very little vanadium alloying of the substrate was obtained
in cycles of either 4 hours at 2000°F or 6 hours at 2100°F, and quite severe
contamination of the columbium and tantalum substrates was metallographically
observed. The precipitate in the columbium substrate appeared to be either
an oxide or nitride phase. The apparent source of the contaminating species
was the vanadium powder, and vanadium is notoriously rich in interstitial
impurities. The titanium precoat was equally ineffective in furthering the
diffusion of tungsten, and it was in fact removed from the substrate surface
during treatment in the tungsten pack by reaction with the pack activator.

The barrier layer coating obviously required protection from oxidation,
and this was accomplished by alloying the surface layer with silicon. To
most effectively serve as a deterrent to diffusion, a barrier layer should
be sufficiently thick that upon siliconizing the layer is not completely
alloyed with the coating elements. Thus, a minimum barrier layer requirement
of 1.5 mils thick was estimated, based upon the known substrate consumption
values obtained when siliconizing pure tungsten. This being the case, and
considering the very slow interdiffusion rates of the refractory metals, the
vacuum pack method did not appear to be a feasible means of forming diffusion

174
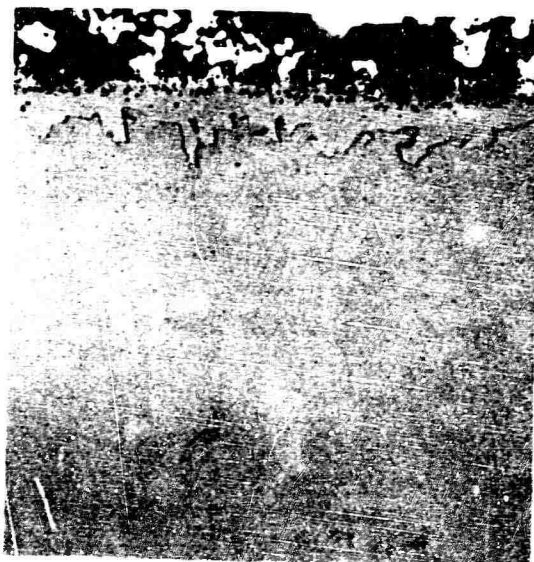
Unalloyed Cb   D-43
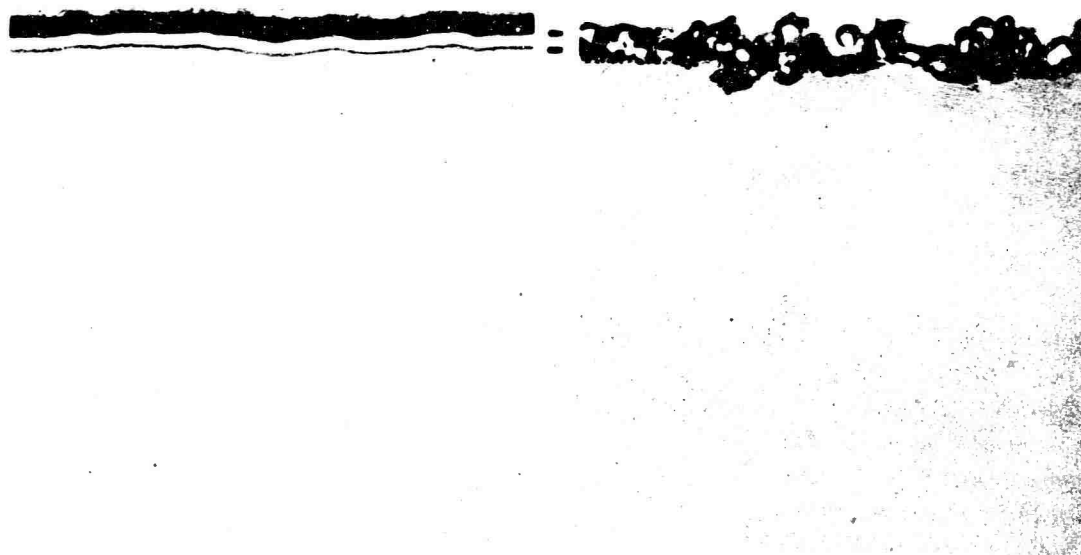
B-66   Ta-10W

Figure 90   Tungsten Alloy Barrier Layer Coatings Formed on Columbium
            and Tantalum Base Substrates in 6 Hours at 2500°F   500X

175

barrier layers on columbium and tantalum.

Although the barrier layers formed by this method were quite thin, it was considered that a series of oxidation tests might demonstrate the potential of the barrier layer approach and also aid in directing the future selection of barrier coating systems. Seventeen coating systems were formed on D-43 and Ta-10W alloy coupons utilizing the parameters described in Figure 91. All of these processing cycles were conducted in the 3" diameter x 8" high retort facility, using NaF + KF pack activation. The coating systems not involving tungsten or molybdenum intermediate layers were prepared as comparative systems for evaluating the effectiveness of the diffusion barrier.

Cyclic oxidation tests (air) were conducted with these specimens utilizing the test conditions outlined in Table 3. These oxidation test data are given in Tables 33 and 34. It should be pointed out initially that direct siliconizing of the Ti or Ti-(W) precoated D-43 and Ta-10W resulted in the formation of a non-adherent silicide coating which cracked and spalled from many of the coupons. The oxidation data from these systems are therefore extremely erratic. Two replicate specimens from each system were evaluated for each condition.

Regarding D-43 alloy, the barrier layer coatings were considerably less protective at oxidation temperatures from 1800-2700°F than were the modified Cr-Ti-Si coatings on this alloy. At 3000°F the barrier layer and modified Cr-Ti-Si coatings (also see Tables 30 and 31) were about equally protective, whereas at 3200°F and above a definite superiority was evidenced by the barrier coatings. The sacrifice of low temperature protective reliability for improved higher temperature protection was not unexpected with the barrier coating systems.

The data presented in Table 33 are too few to permit any specific conclusions, however, certain trends in coating superiority can be observed. With few exceptions, the best performance at 3000°F and above was exhibited by coatings containing tungsten. Vanadium and titanium prealloying were definitely beneficial, although this improvement was not in fact associated with a thicker barrier. Since the tungsten and molybdenum barriers were quite thin, and were therefore entirely alloyed with silicon during the final siliconizing cycle, all of the constituents present in these systems served essentially as silicide modifiers rather than barrier layers. However, the appreciable alloying of the silicide coatings with tungsten and molybdenum undoubtedly impeded the outward diffusion of columbium through the silicide, thereby providing some barrier effect. Typical protective lives of several of these tungsten (vanadium and titanium) containing systems were 4-7 hours at 3000°F, 3 to >9 hours at 3200°F and 2-4 hours at 3300°F.

All of the coating systems applied on Ta-10W alloy were less oxidation protective than the corresponding systems on D-43 alloy, and were in general quite ineffective in protecting the tantalum alloy. At 1800°F the protective lives of these coatings generally did not exceed 50 hours, and at 2500 and

176
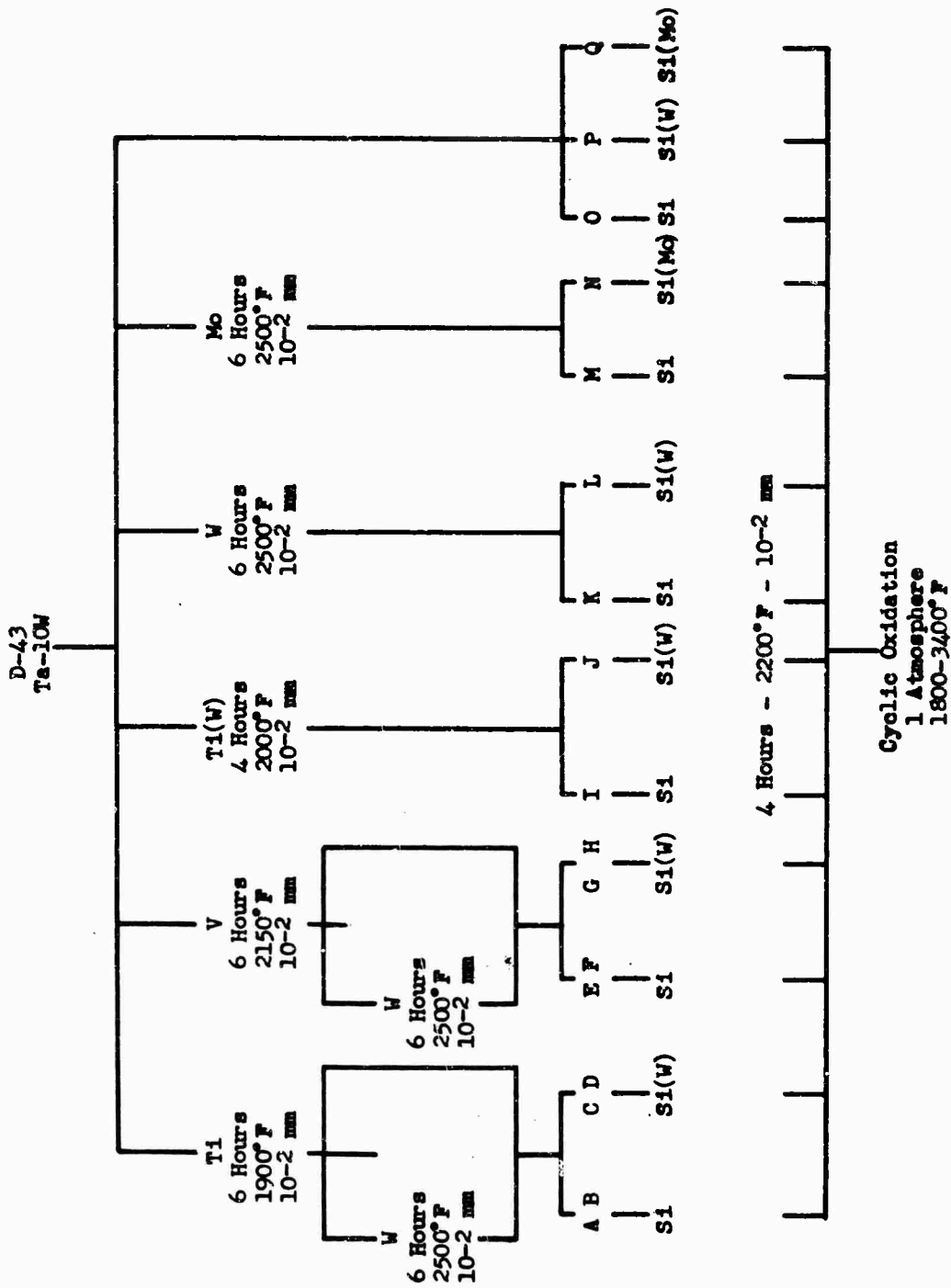
Figure 91 Schematic Showing the Barrier Layer Coating Systems Evaluated on D-43 and Ta-10W Alloys

177

TABLE 33

Cyclic Oxidation Test Results for Barrier Coating Systems Formed on D-43 Alloy

Designation	Coating System(b)	Coating Thickness Mils	Protective Life - Hours(a)					
			1800°F	2500°F	2700°F	3000°F	3200°F	3300°F
A	Ti-Si	3.2-3.4	>168(2)	26,26	1,4	9	1.0	<0.1,0.3
B	Ti-W-Si	3.0-3.2	>168(2)	8,24	2,2	4	3.7	0.5,2.0
C	Ti-Si(W)	3.2-3.6	74,>168	24,26	2,9	1.5,2	0.8	0.2,0.3
D	Ti-W-Si(W)	3.2-4.0	>168(2)	24,24	2,2	4,4	>8.0	0.8,4.0
E	V-Si	2.4-2.5	51,51	24,24	1,2	1,4.5	>9.0	0.3,0.6
F	V-W-Si	3.2-3.6	27,>168	7,8	2,2	4.5,5	7.3	0.8,4.2
G	V-Si(W)	2.4-2.6	74,74	8,24	2,2	2,3.5	0.3	0.6,3.0
H	V-W-Si(W)	3.6-4.0	29,72	8,24	2,3	3.5,7	3.8	0.4,3.6
I	W-Si	2.2-2.3	>168(2)	24,24	1,1	2,4	3.6	0.5,2.2
J	W-Si(W)	2.2-4.2	74,>168	24,24	1,1	1,4	>3.0	0.3,3.6
K	Mo-Si	2.8-3.6	>168(2)	24,24	1,3	1,1.5	1.2	0.3,0.4
L	Mo-Si(Mo)	2.6-2.7	24,29	24,24	1,2	0.5,0.5	0.4	0.6,0.6
M	Ti(W)-Si	0.2-2.0	3,7	3,24	2,2	0.5,0.5	0.3	0.1,0.1
N	Ti(W)-Si(W)	0.6-3.2	29,48	1,1	2,2	0.5,0.5	0.2	<0.1,0.1
O	Si	2.8-3.2	48,50	4,4	1,2	0.5,1	>7.0	0.9,1.3
P	Si(W)	2.2-2.4	>168(2)	4,4	1,1	1,1	5.2	0.2,3.0
Q	Si(Mo)	2.4-2.5	>168(2)	4,3	1,1	0.5,0.5	>7.0	0.2,0.3

(a) See Table 3 for oxidation test procedures

(b) See Figure 91 for processing conditions

178

TABLE 34

Cyclic Oxidation Test Results for Barrier Layer Coatings on Ta-10W Alloy

Designation	Coating System	Coating Thickness Mils	Protective Life(a)						
			Hours				Minutes		
			1800°F	2500°F	2700°F	3000°F	3200°F	3300°F	3500°F
A	T1-S1	3.2-3.3	7,7	3,24	4,5	2,7 1/2	20	10	2
B	T1-N-S1	2.8-4.6	24,24	5,6	3,3	2,2	12	10	3
C	T1-S1(W)	1.8-2.4	7,24	6,8	5,4	1,1	5	5	1
D	T1-N-S1(W)	4.0-4.2	6,24	6,6	3,3	1 1/2,1	17	10	1
E	V-S1	2.6-3.2	130,150	7,7	3,4	1,1	15	6	8
F	V-N-S1	2.4-3.0	8,48	3,6	4,6	1,1	10	10	1
G	V-S1(W)	2.0-2.4	55,24	7,7	3,4	1,1	12	8	9
H	V-N-S1(W)	2.4-2.6	3,3	5,6	4,3	1/2,1 1/2	18	15	9
I	N-S1	2.8-3.0	29,24	6,6	1,4	1,1 1/2	14	10	5
J	N-S1(W)	2.8-3.4	7,24	7,6	3,1	1 1/2,2	20	9	5
K	Mo-S1	2.4-2.6	3,3	3,3	1,2	1/2,1	8	5	3
L	Mo-S1(Mo)	2.4-2.6	3,2	1,1	2,2	1/2,1/2	4	6	1
M	T1(W)-S1	0-3.6	5,3	1,3	1,2	1/2,1/2	3	4	2
N	T1(W)-S1(W)	0.2-3.2	4,5	1,4	2,2	1/2,1/2	3	4	2
O	S1	2.0-2.4	48,50	5,5	2,2	1/2,1	14	10	6
P	S1(W)	2.4-2.6	24,50	6,6	2,2	1/2,1/2	20	10	3
Q	S1(Mo)	2.0-2.2	29,50	5,5	2,2	1/2,1/2	15	9	4

(a) See Table 3 for oxidation test procedures

(b) See Figure 91 for processing conditions

179

2700°F the protective lives were less than 8 hours. With one exception, the maximum protective life was 2 hours at 3000°F, 20 minutes at 3200°F, 15 minutes at 3300°F and 9 minutes at 3500°F. Silicide coatings are relatively protective on columbium base materials, and the alloying effect of the barrier layer elements improved the silicide performance on D-43 alloy. Tantalum silicides are considerably less oxidation resistant than columbium disilicide, and the absence of an effective barrier layer reflected in the very poor performance of the coatings on the tantalum alloy.

In general, the efforts to form the diffusion barriers by the vacuum pack method were unsuccessful. Although there were individual coupons which displayed attractive protective lives on the columbium substrate at 3200 and 3300°F, the absence of an effective diffusion barrier was clearly demonstrated by the performance of the analogous coating systems on tantalum. As stated previously, the vacuum pack technique does not appear to be a practical means of forming tungsten or molybdenum barrier layers of columbium or tantalum substrates.

8.2.2 Chemical Vapor Deposition Technique

Several sources were explored in an effort to acquire vapor deposited tungsten coatings on columbium and tantalum substrates. In addition to the experimental work conducted at TRW, coatings were sought from the National Bureau of Standards Laboratory, Ethyl Corporation and General Telephone and Electronics Corporation.

Several D-43 and Ta-10W alloy coupons were submitted to the National Bureau of Standards Laboratory for tungsten plating by the hydrogen reduction of tungsten hexachloride. This work was conducted for TRW under Air Force Contract AF 33(615)-65-05. Several D-43 alloy coupons were plated with 1-2 mil coatings of tungsten; and attempts were made at TRW to diffusion bond the tungsten and substrate components by a high temperature heat treatment. Diffusion cycles of 4 hours at 2500°F were conducted in vacuum and in atmospheres of hydrogen and argon. In all cases the tungsten coating cracked and spalled from the columbium substrate, and metallographic examination indicated bonding occurred only in a few isolated areas. The tungsten coatings were vapor deposited on the columbium coupons at 1100-1200°F in an atmosphere of hydrogen, and the solubility of columbium for hydrogen is approximately 15 a/o in this temperature range. The degree of hydriding of the columbium during the tungsten plating process was not known. However, since tungsten is an excellent hydrogen diffusion barrier[14], rejection and expansion of the dissolved hydrogen upon heating to the 2500°F diffusion temperature apparently generated sufficient internal pressure to rupture the tungsten coating. Hydriding of the substrate material definitely precludes the utilization of a low temperature (600-1200°F) hydrogen reduction process for the vapor deposition of tungsten on columbium or tantalum. The greater expansion coefficient of columbium relative to tungsten also contributed to a tendency towards spalling of the tungsten deposit. NBS attempts to deposit adherent tungsten coatings on Ta-10W alloy coupons were unsuccessful.

Ten Ta-10W alloy coupons were tungsten coated for TRW by the Ethyl Corporation, employing the thermal decomposition of tungsten hexacarbonyl. This work was performed for TRW under Contract AF 33(657)-11247. The plating temperature was 550°C (1022°F), and the coupons were plated in two steps. Ethyl analyzed one coated specimen by an electron diffraction technique. It was found that the coating on one side of the coupon was 65-75 mol % tungsten and 25 mol % W_2C, whereas the opposite side analyzed the reverse composition(15). Vacuum diffusion bonding treatments performed on these coatings at 2300 and 2500°F resulted in gross cracking and spalling of the tungsten-tungsten carbide deposits. Attempts to silicide the coatings without prior diffusion bonding were equally unsuccessful, again resulting in severe spalling of the coatings, and the efforts to utilize the coupons were abandoned. Figure 92 shows photomicrographs of the coatings on Ta-10W alloy, before and after siliciding. The apparent carburization of the tantalum surface is evident beneath the deposit.

Sixteen Ta-10W alloy coupons were tungsten plated for TRW by General Telephone and Electronics Laboratories, employing the thermal decomposition of $WC1_6$ (1500-2000°F). A post vacuum diffusion treatment of approximately 1 hour at 2400°F was performed to diffusion bond the coating and substrate components. Metallographic analysis of a section from one of these coupons evidenced virtually a continuous void at the tungsten coating-substrate interface; however, the coatings display no external cracks or tendency to spall. The thickness of the tungsten coating on the sectioned coupon was 1.5 mils. The fifteen remaining coupons were Si-(W) coated for 4 hours at 2150°F, resulting in a tungsten disilicide coating approximately 2 mils thick and a residual tungsten layer 0.7-0.8 mils thick. No spalling or cracking of the duplex coatings was observed. Figure 93 presents photomicrographs showing the tungsten coating before and after siliciding.

Cyclic oxidation tests were performed on the fifteen specimens at temperatures from 1800 to 3500°F. These data are presented in Table 35. It was found that after exposure at 3000°F and above for any significant length of time, upon subsequent cooling to room temperature a portion of the duplex coating would spall from the specimen edges. Owing to this mismatch in thermal expansion of the various coating layers, intermediate cooling of the test coupons to room temperature would have precluded any real evaluation of the high temperature protective capabilities of the coatings. Therefore, the specimens were cooled only to approximately 600-800°F during cycling for visual inspection.

At 1800 and 2500°F the coatings failed after 2 and 5 hours respectively, presumably as a result of the "pest" type phenomenon characteristic of silicide coatings. At 3000 and 3200°F the tests were terminated prior to the evidence of coating failure, and lives exceeding 11 and 16 hours at 3000°F and 9.5 and 12 hours at 3200°F were recorded. At 3300°F one coupon failed in 3.5 hours, whereas the second coupon failed after 4 hours as a result of spalling which was incurred upon cooling the specimen to room temperature. The coating protective lives ranged from 0.3 to 2.0 hours

181
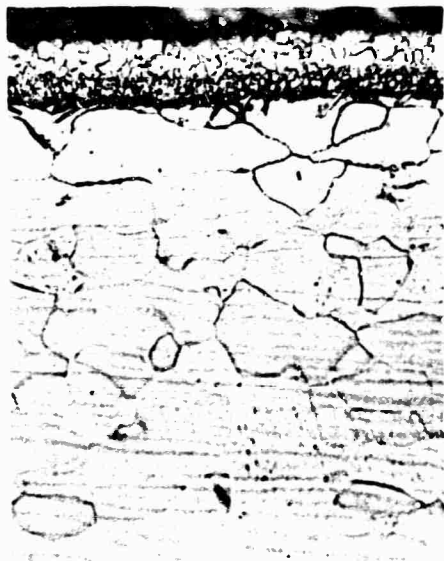
Tungsten Plated - Ethyl   Tungsten + Silicon

Uncoated Ta-10W

Figure 92   Ta-10W Alloy - Uncoated, As Tungsten Plated by Ethyl Corporation
            and After Siliconizing   500X

182

Tungsten Deposit

Void

Ta-10W Substrate

As Tungsten Plated - GT&E

Silicide Coating

Residual Tungsten

Void
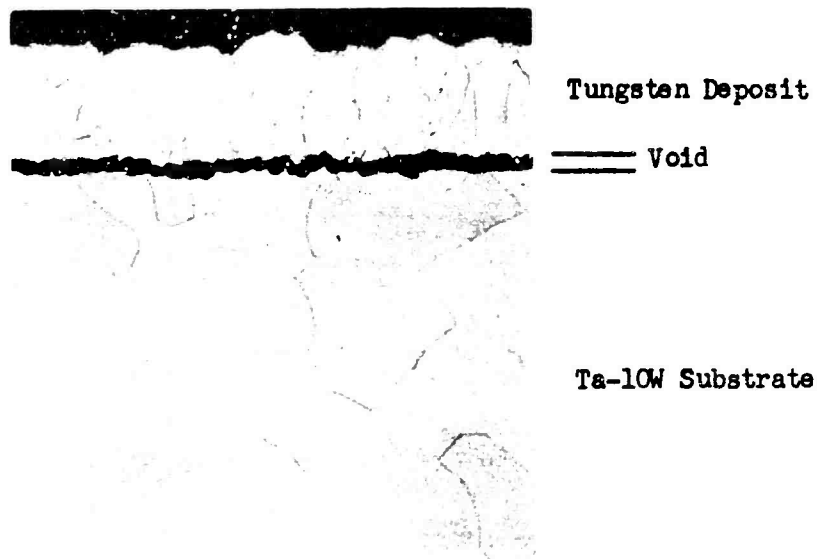
Ta-10W Substrate
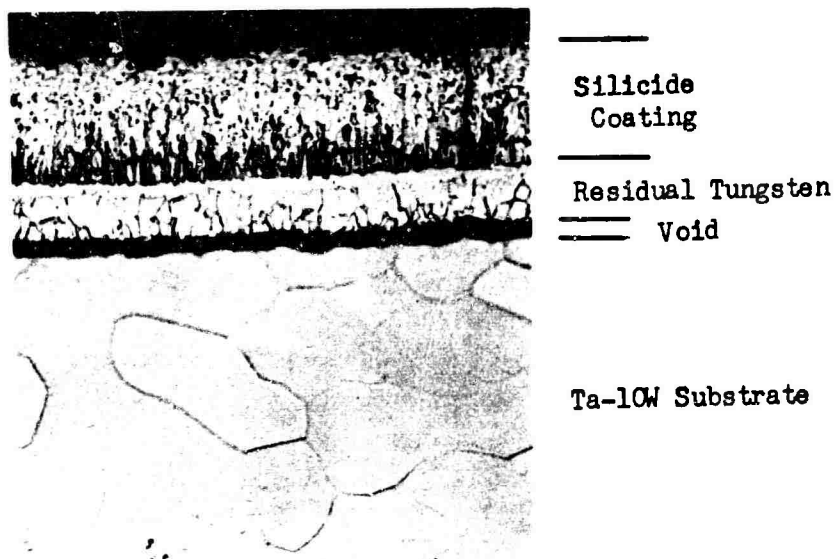
Tungsten Plate + Silicide Coating

Figure 93   Ta-10W Alloy - As Tungsten Plated by GT&E and After Siliconizing by TRW
500X

183

TABLE 35

Cyclic Oxidation Properties of Barrier Coating System
(GT&E Tungsten + TRW Si-(W)) on Ta-10W Alloy

Temperature - °F	Protective Life - Hours[a]
1800	2
2500	5
3000	> 11, > 16[b]
3200	> 9.5, > 12[b]
3300	3.5, > 4[c]
3400	0.3, 1, 2
3500	0.5, 1, 3
3600	< 0.1

(a) Cyclic oxidation test procedure - See Table 3

(b) Tests terminated prior to failure

(c) Specimen cooled to room temperature - coating spalled on coupon edges

at 3400°F and 0.5 to 3.0 hours at 3500°F. The temperature limit of the coating system appeared to be in the range 3500-3600°F, based on the observed melting of the coating at approximately 3600°F. At all test temperatures of 3000°F and above a very glassy oxide formed on the coating surface during exposure, and this glassy phase varied in thickness and in color with exposure time and temperature.

Figures 94 and 95 show photomicrographs of several of the coatings after various exposures. No effort was made to identify the various phases formed as a result of these high temperature exposures, however, certain speculations can be made. Two hours at 1800°F had little effect on the microstructures of the tungsten disilicide coating and the interposed pure tungsten coating layer. Five hours at 2500°F resulted in effective diffusion bonding of the duplex coating to the tantalum alloy substrate, in addition to permitting silicon diffusion through the tungsten barrier layer. The etchant stained layer adjacent to the substrate is probably W_5Si_3, formed at the expense of the tungsten barrier layer. Exposure at 3000°F and above resulted in the formation of a thick glassy oxide phase on the coating surface. The WSi_2 phase is observed to be gradually depleted of silicon during the oxidation exposure resulting in conversion of the disilicide to the etchant stained W_5Si_3 phase (outer layer). The diffusion bands adjacent to the substrate are apparently lower silicides of the tantalum-silicon system, probably Ta_5Si_3 and Ta_2Si. These latter phases are quite oxidation resistant in comparison to the tantalum matrix, as evidenced by the stability of the phases in contact with tantalum oxide (Figure 95).

The performance of these coatings at temperatures of 3000°F and above was very encouraging, and clearly demonstrated the excellent protective potential of the barrier layer coating system. In most cases the shorter failure times at temperatures above 3200°F were associated with reactions between the coatings and support materials. The test coupons were supported on Si-(W) coated molybdenum coupons (sacrificial pads - see Table 3) which failed after a short time at 3300°F and above. The corrosive effect of the vaporizing MoO_3 was detrimental to the performance of the tungsten disilicide coatings.

Late in the program an effort was initiated at TRW to chemically deposit tungsten coatings on columbium and tantalum alloy substrates. Layers of tungsten were deposited on D-43 columbium alloy specimens in a laboratory scale barrel coating reactor utilizing the thermal decomposition of tungsten hexachloride (WCl_6). Metered quantities of argon and chlorine were passed through tungsten chips and coarse tungsten powder at 750°C (1382°F), forming gaseous WCl_6. The gaseous WCl_6 and argon carrier gas were then introduced into the rotating quartz "barrel", where reduction of the halide compound to metallic tungsten occurred. Four vanes in the periphery of the continuously rotating barrel served to tumble the samples during the deposition reaction. This tumbling action ensured uniform deposition over the entire specimen surface.

185
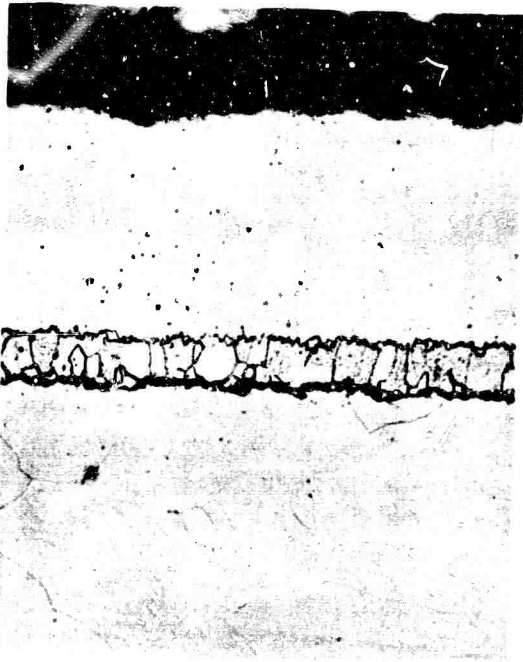
2 Hours   1800° F   5 Hours   2500° F

16 Hours   3000° F   12 Hours   3200° F

Figure 94   Microstructures of Barrier Coatings on Ta-10W Alloy - GT&E
Tungsten + Si(W) - After Various Elevated Temperature
Exposures in Air

                                                           500X

2 Hours   3400° F   500X   1/2 Hour   3500° F   500X

Oxidized
Substrate

Ta-10W
Substrate
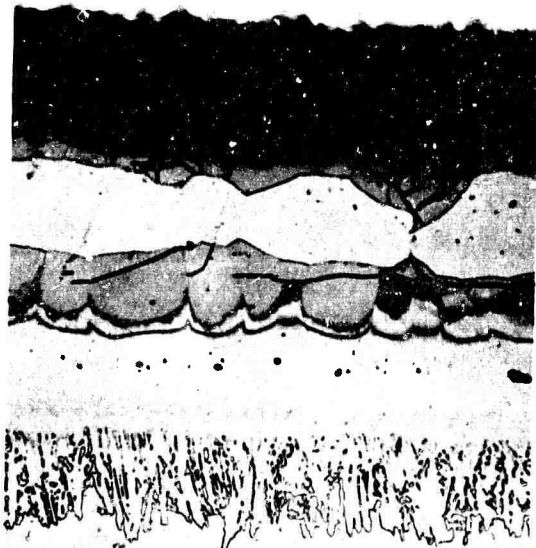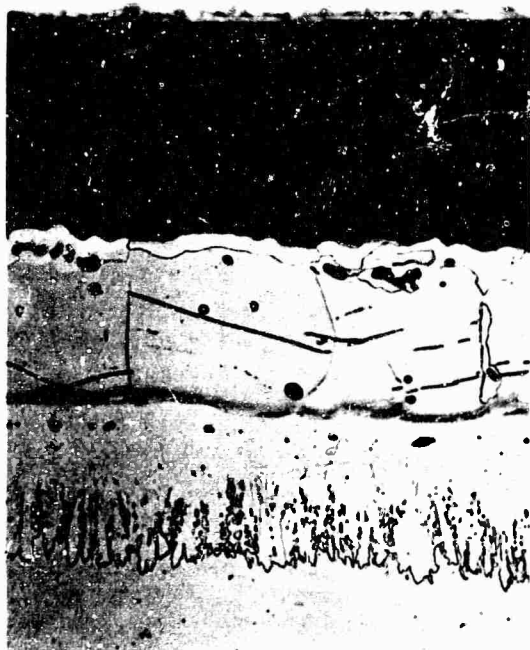
16 Hours   3000° F   250X

Figure 95   Microstructures of Barrier Coatings on Ta-10W Alloy - GT&E
             Tungsten + Si-(W) - After Various Elevated Temperature
             Exposures in Air

187

Sixteen D-43 columbium alloy specimens, 1/2" x 1/2" x 60 mil were coated with approximately 1 mil of tungsten. The deposition conditions were:

a) Temperature - 1050°C (1922°F)

b) Pressure - one atmosphere

c) Halide generator temperature - 750°C (1382°F)

d) Moles argon/moles WCl_6 - 50/1

e) Flow rate of WCl_6 equivalent to a transfer of 6 grams tungsten/hour

f) Time - 3 hours

The tungsten deposits thus formed were quite porous, however, the coupons were siliconized for oxidation evaluation. It was observed metallographically that the entire thin tungsten layer was converted to tungsten disilicide, and silicon penetration of the columbium substrate was also evident. Oxidation tests were conducted with several of these coupons at 3000 and 3200°F, however, without an adequate barrier layer the coatings failed to survive 1 hour exposure. Based on this poor performance of several representative coupons the oxidation tests on the remaining lot were discontinued. Due to the late entry of this work into the program there was not sufficient time remaining to improve the tungsten barrier layers produced by the TRW vapor deposition technique.

It is concluded from this barrier layer coating effort that the proposed duplex coating system has excellent potential for the protection of columbium and tantalum base materials at temperatures above 3000°F. Additional developmental effort is certainly required in the chemical vapor deposition of tungsten, however, the GT&E success in this area adequately demonstrates the process feasibility. The TRW experience in the development of protective coatings for tungsten should be invaluable in expediting the advancement of the duplex-barrier coating systems for tantalum and columbium.

9. CONCLUSIONS

1. The coating formed on columbium alloys in the Cr-Ti coating cycle consists of a Laves phase of the form $(Cb,Ti)Cr_2$, overlaying a matrix solid solution of chromium and titanium in columbium.

2. Siliconizing Cr-Ti coated columbium results in the formation of a disilicide coating of the form $(Cb,Cr,Ti...)Si_2$.

3. Exposure of the Cr-Ti-Si coating in air (one atmosphere) at temperatures of 2000°F and above results in the simultaneous oxidation of the

coating and the loss of chromium from the coating via the vaporization of the element and/or the oxide.

4. Reduced pressure (air) exposure of the Cr-Ti-Si coating at 2500°F and above results in the vaporization loss of both chromium and silicon (SiO) from the coating, rapidly leading to enrichment of the remaining disilicide coating and surface oxide in columbium and titanium.

5. Three factors contributing to failure (non-defect oriented) of the Cr-Ti-Si system are:

   a) evaporation of chromium and silicon (reduced pressure) from the coating

   b) enrichment of the disilicide and the surface with columbium, thereby rendering the oxide non-protective

   c) depletion of chromium and titanium from solid solution in the matrix, thereby rendering the substrate susceptible to oxidation at the base of thermal cycling cracks

6. The 97.5% probable protective life (99% confidence level) of the Cr-Ti-Si coating on D-43 and B-66 alloys is 59 and 82 hours respectively, under the conditions of cyclic oxidation (air at one atmosphere). The corresponding mean protective lives are 109 and 139 hours. At 1800°F the Cr-Ti-Si coating on these alloys demonstrated a 100% probable protective life up to 144 hours of cyclic oxidation (test limit). The mean protective life (Weibull) of the Cr-Ti-Si coating on D-43 and B-66 alloys at 2700°F is 36 and 32 hours, respectively.

7. Helium backfilling (150 mm) of the evacuated furnace chamber during heat-up of the granular coating pack markedly increases the internal heat-up rate of the pack.

8. A Cr-Ti-Si coating, comparable to that of the analogous vacuum pack coating, can be formed on columbium base materials by a laboratory scale slurry-diffusion process.

9. Exposure of the Cr-Ti-Si coating in air under the conditions of a slow thermal cycle from 800 to 2500°F is a more severe test criteria than conventional thermal cycling (cyclic oxidation).

10. Modification of the existing Cr-Ti-Si system for higher temperature performance capability, by the addition of higher melting point elements (W, Mo, etc.) to the silicon coating pack, did not prove feasible in this work.

11. The duplex barrier layer coating system, consisting of an interposed barrier layer of tungsten between the columbium or tantalum substrate and a protective silicide coating, has excellent potential for use at temperatures to 3500°F.

12. Based on the difficulties encountered in obtaining chemically vapor deposited tungsten coatings on columbium and tantalum, it is apparent that a great deal of further process development effort is required in this area.

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13. ABSTRACT A program was conducted to study coatings for the protection of columbium and tantalum base alloys. Four major areas were investigated: (1) the basic factors associated with the formation and protection of the vacuum pack Cr-Ti-Si coating; (2) the laboratory scale development of a spray-diffusion process for applying the Cr-Ti-Si coating; (3) the development of metallic coatings for the protection of columbium and tantalum materials at temperatures to 3500°F; and (4) evaluation of various coating-base metal systems studied in the program.

In Phase I Cr-Ti-Si coatings on columbium alloys were studied in the as-formed condition and after reduced pressure and one atmosphere exposures. Electron microprobe, light and electron microscopy, and X-ray diffraction data are presented.

Phase II resulted in the laboratory scale development of a spray-diffusion process for producing Cr-Ti-Si coatings on columbium base materials are clean.

Two concepts were explored in the investigation of coatings for the 2700-3500°F protection of columbium and tantalum materials: (1) alloy modification of the existing Cr-Ti-Si coating with tungsten and molybdenum and (2) a barrier layer approach involving interposing a bonded metallic layer of tungsten between the columbium or tantalum substrate and a protective silicide coating.

A property evaluation of various coating-base systems was conducted in the final phase of the program. Metallographic, oxidation and mechanical property test data are presented for various pack and slurry processed Cr-Ti-Si coatings on columbium and tantalum materials. Statistical and Weibull analyses are presented.

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